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# METALS and ALLOYS

## The Magazine of Metallurgical Engineering

**PRODUCTION • FABRICATION • TREATMENT • APPLICATION**

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# HOW TWO

**EVERYTHING IDENTICAL but the steel.**

*But the gears at the right made of a special grade of U·S·S Carilloy Alloy Steel—will scuff less, run more quietly, and cost 12½¢ less per set. A typical result of close cooperation between our metallurgists and yours.*

E. Eng. Lib.
Fapod

CRANKSHAFTS AND OTHER PARTS

# Surface Hardened by Inductive Heat

## by Edwin F. Cone

IN A LARGE PLANT in Cleveland, the bearing surfaces of steel crankshafts are being satisfactorily hardened in from 1.8 to 6.0 seconds, depending on the steel being treated and the bearing sizes. And this is being accomplished on a large scale—practically mass production.

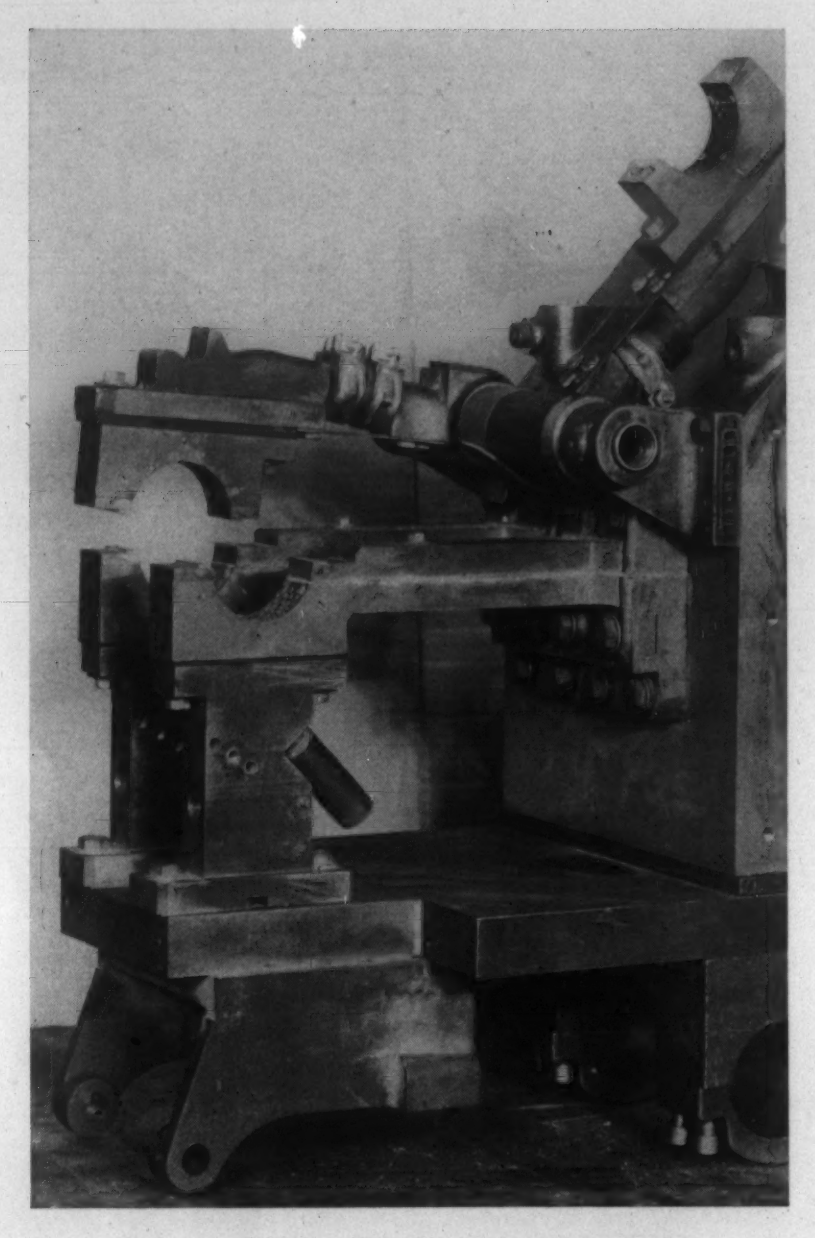
Had any one predicted, only a few years ago, that this would have been possible, he would have been laughed out of court.

The new method, as compared with the older ones, annihilates time, obviates distortion, and is attended with no scaling. The development of inductive heat, or heat by electric induction, has made this remarkable achievement possible.

Recognizing the great value of this principle of heating by induction, The Ohio Crankshaft Co., Cleveland, has applied it with some modifications to its operations, and phenomenal success has attended these efforts. The process has been named the "Tocco" process.

Until the development and perfection of the electric inductive method of heating steel previous to hardening by quenching and drawing, there were several established processes. These include carburizing, cyaniding, nitriding, Chapmanizing and so on. The use of the acetylene torch for this purpose is a more modern process. The object of all methods is to produce a hard surface on a soft, tough metal core.

*Tunnel Line for Tocco Hardening Crankshafts.*

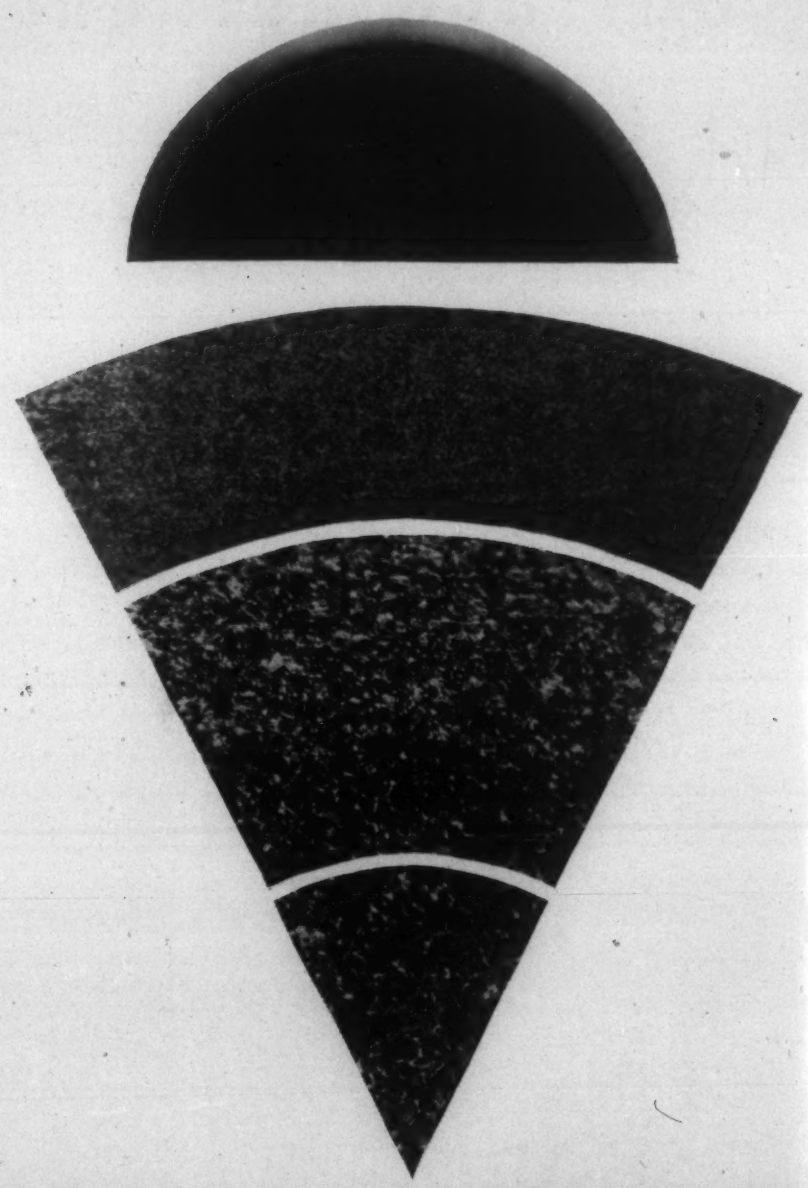


*Inductor Blocks Showing Quenching Holes.*

All of these older methods involve the absorption of other elements into the surface to be hardened—a process of diffusion in solid metals. In all of them time is an important factor and in some of them distortion as well as scaling is a disadvantage.

## Inductive Electric Heating

The development by the Ajax Electrothermic Corp., Trenton, N. J., of the principle of inductive electric heating—the rapid absorption of heat by induced electricity—

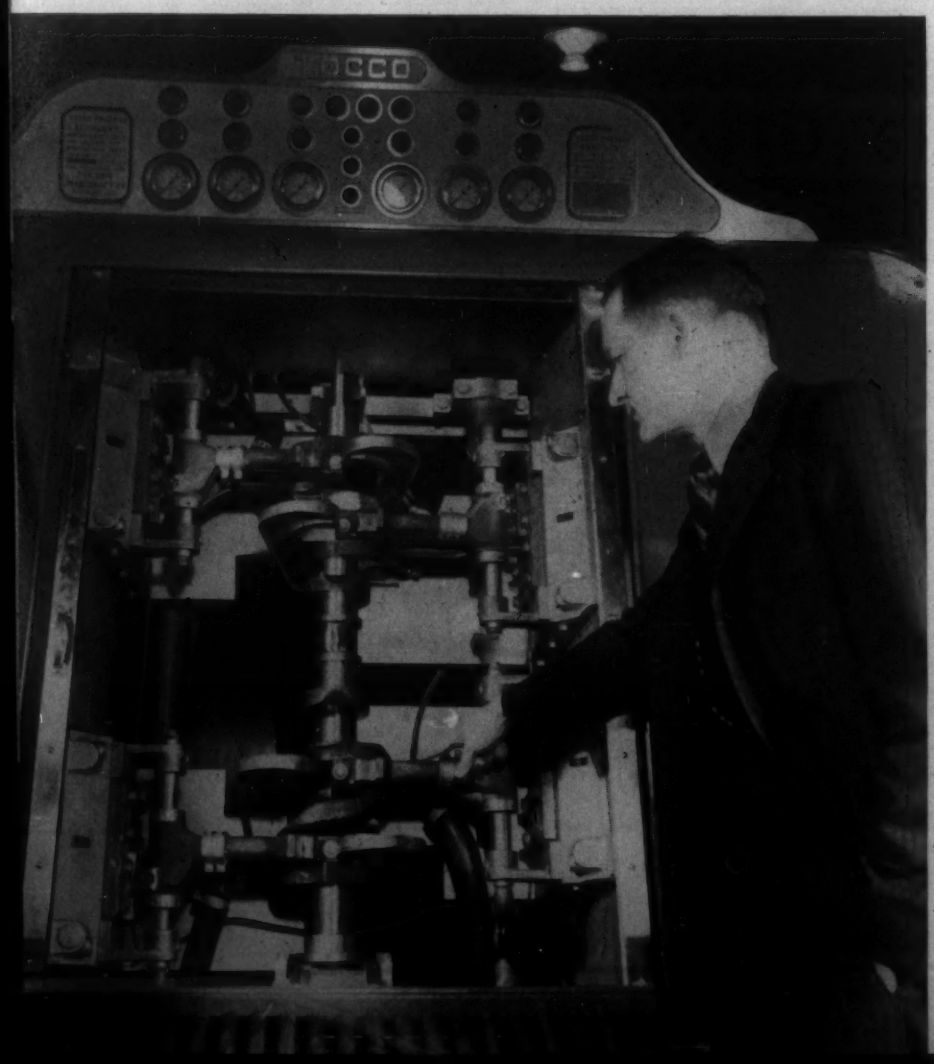


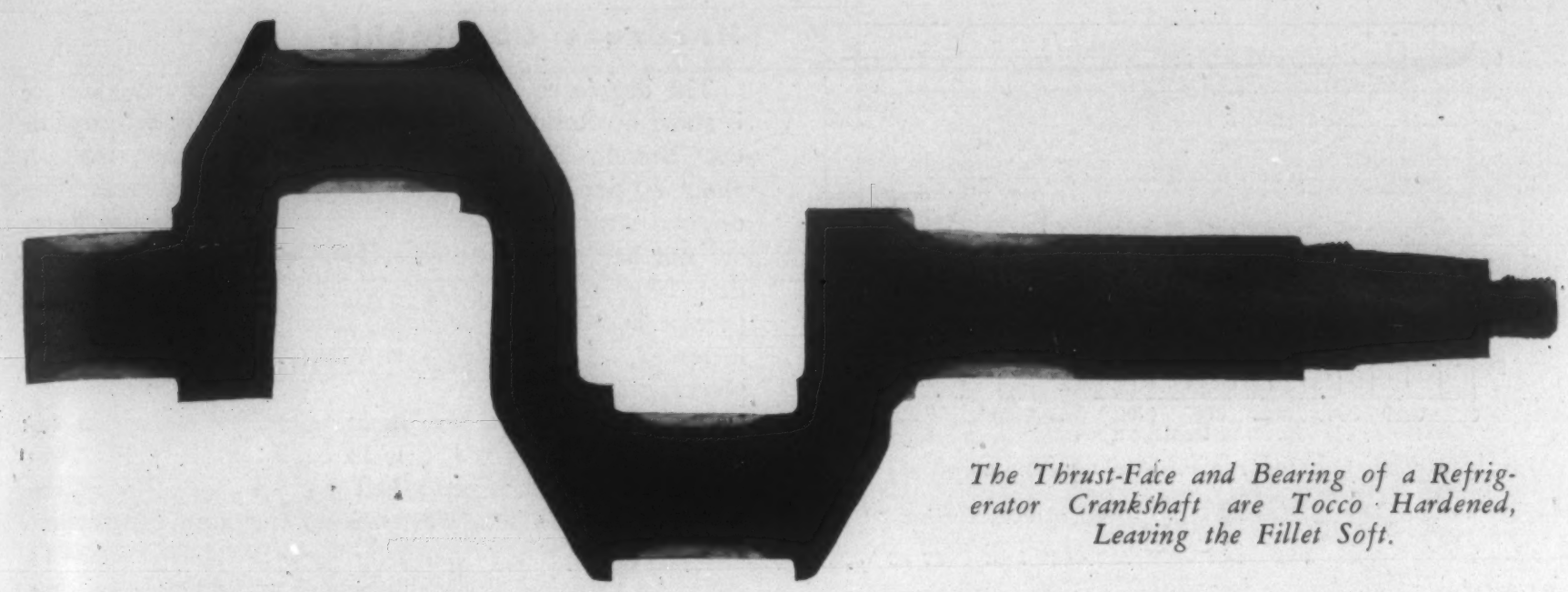
*Typical Microstructure of Tocco Hardened Bearing. Note gradual blending of hardened area into core through the demarcation zone. Upper cut is a section of a normalized 0.53 carbon steel. The three parts below represent the surface, the gradation zone and the core respectively.*

has revolutionized some metallurgical and heat-treating processes. The induction furnace for producing steel is an outstanding and successfully established example. A large measure of credit for the development and applications of induced electric heat is widely recognized as due to Dr. E. F. Northrup, vice-president and technical advisor of the Trenton company.

For years the Ohio Crankshaft Co. had been producing hardened bearing surfaces by some of the old methods, some of them requiring time cycles of as many as 90 hrs. Most of the readers of this article are familiar with some of the disadvantages of the old established methods of hardening—distortion, necessary straightening, cracking of the shaft in the fillets on straightening, high grinding costs since more stock had to be left for grinding to compensate

*Closeup of Left Hand Machine of a Vertical Unit.*





*The Thrust-Face and Bearing of a Refrigerator Crankshaft are Tocco Hardened, Leaving the Fillet Soft.*

for some distortion, and grinding checks due to lack of uniformity of the structure and depth of the case.

As the types of automotive transportation developed, including the Diesel engine, with the augmented bearing pressures and speed and with the advent also of the newer and harder bearing alloys,—copper-lead, cadmium-silver, and cadmium-nickel,—a crankshaft that would stand these severer operating conditions was a necessity. The harder bearings were actually wearing the crankshaft metal which was limited as to hardness obtainable by the then hardening methods available. This need prompted the officials of the Cleveland company to search for a new method of surface hardening.

There was a demand for a crankshaft which would be capable of operating many thousands of miles without a bearing failure or even a bearing adjustment.

## "Tocco" Process Developed

The results of the company's research and experimentation, which involved many very difficult problems, are known to many—the use of inductive electric heat carefully and automatically controlled. The story of this development was ably presented in a paper "Differential Hardening by Induction" by M. A. Tran of the Park Drop Forge Co., and W. E. Benninghoff of The Ohio Crankshaft Co., at the National Metal Congress in Cleveland in October, 1936. At the National Metal Exposition, held at the same time, the display of this process was a large center of interest.

It is not necessary here to describe in detail the process, but it is appropriate to present a few essential facts for the benefit of those not familiar with them, and then to discuss a few metallurgical points of interest.

As to the process, a high frequency current of 2000 cycles is passed through an inductor block. This block surrounds but does not touch the bearing to be hardened. A very strong magnetic field is produced by this current which cuts the bearing surface through a small air gap and induces eddy currents in the bearing surface. This field also creates hysteresis losses in the bearing surface. Heat is therefore generated in the steel surface by the combined eddy current and hysteresis losses. The inductor block remains comparatively cool.

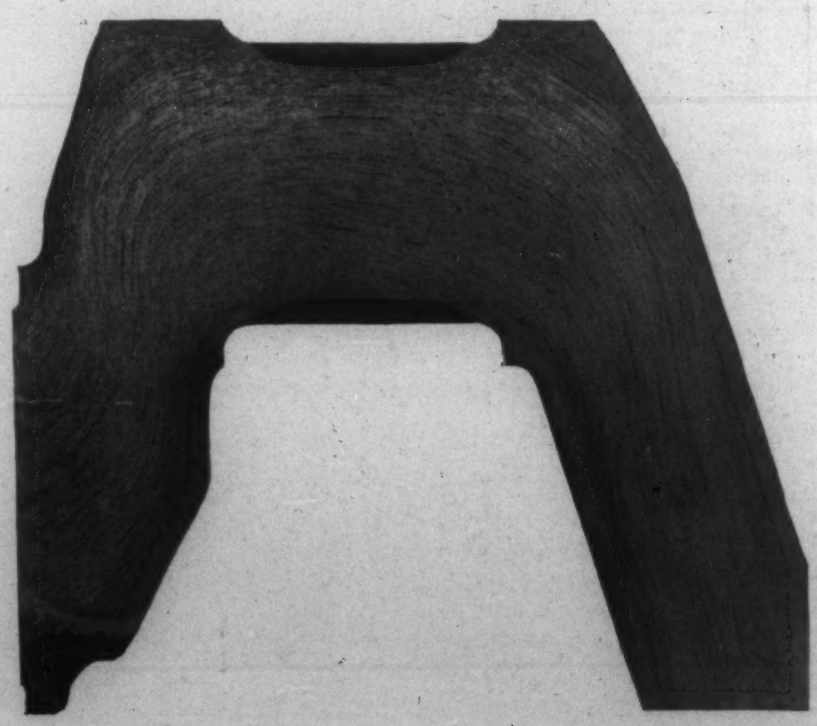
The surface of the steel is not over-heated; due to the inherent reaction of the steel as its temperature rises, the heating effect decreases as the critical point of the steel is approached. Continued application of power would only cause the heat to be generated further in towards the center of the shaft. By pressure spraying through orifices on the inner surface of the blocks, instantaneous quenching results.

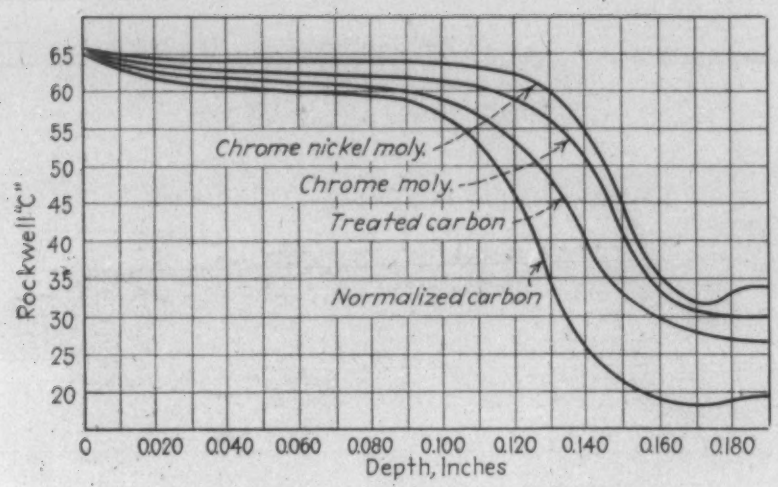
## Some Metallurgical Features

As to certain metallurgical features—several grades of steel are being hardened by the Tocco process. The types being predominantly used are a modified SAE 1050. It is heat treated or air quenched so as to assure maximum ductility consistent with the physical properties desired. The process, however, is not limited to this steel, since a wide range of steels both alloy and carbon are being successfully hardened.

As to grain size—a steel with a McQuaid-Ehn rating of 6 to 8 is preferred, one that in treating produces a martensitic structure in the hardened zone without checking. The steel should also be heat treated to a predominantly sorbitic structure or air quenched to obtain a grain size that approaches the heat-treated structure. By observing these

*Typical Tocco Hardened Crankpin Bearing. Note absence of heating in the fillets.*






*Graph of Hardness Plotted against Depth.*

conditions, a good bond between the case and core as well as successful hardening is assured.

The shaft with the steel in the satisfactory condition stipulated is then machined up to the point of final grinding—from 0.015 to 0.025 in. of stock is left on the bearing diameters and 0.008 to 0.012 in. left on the bearing widths. The shaft is then subjected to the Tocco hardening process, then drawn at a low temperature and finish ground.

During the process the bearing surface is heated to the quenching temperature for a depth of approximately 1/8 in. in from 1.8 to 6.0 secs., as already stated, and the rate of power input and length of time it is applied varies with the different sizes of bearings and with different steels. There is no scaling or pitting of the bearing surfaces because the speed of the heating cycle is measured in split seconds. All the control factors are automatic—power input, length of heating cycle, quenching pressure and time of quenching.

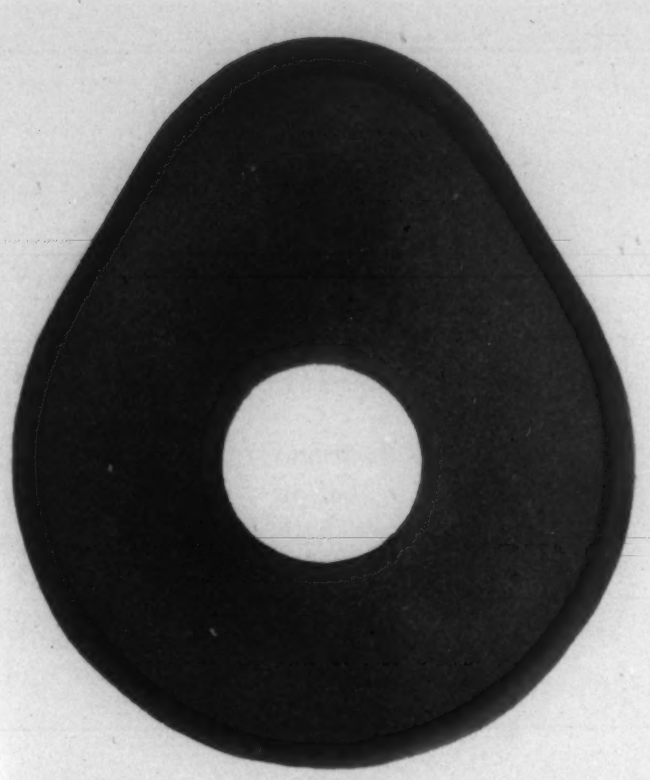
## Hardness Obtainable

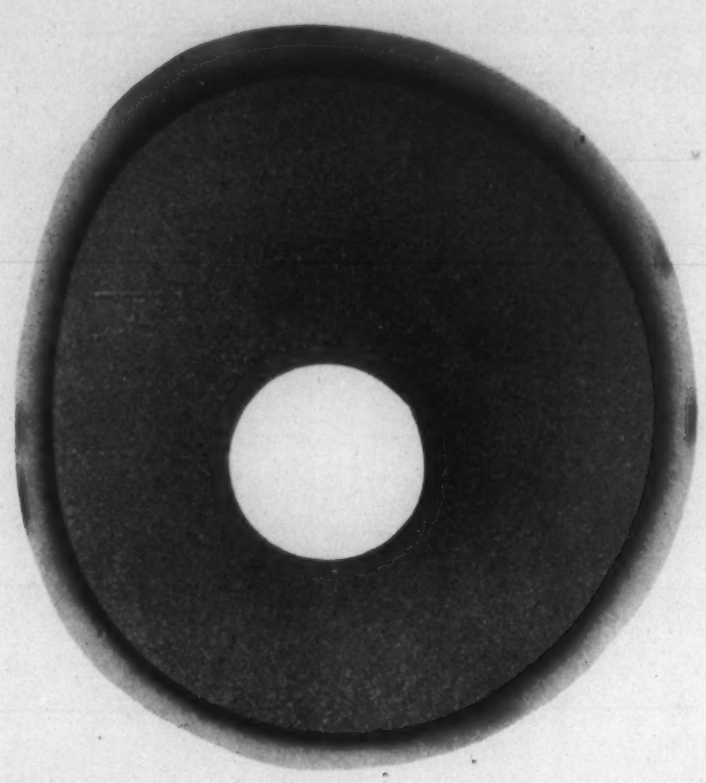
The degree of hardness obtained in the bearing surface is about 60 Rockwell C or approximately 85 Scleroscope or 600 Brinell. This high hardness is maintained through about 80 per cent of the depth of the hardened area. The original structure in the fillets is not changed—the fillets are not hardened but left in their original ductile condition. Nor is the core affected. This is pointed to as important because stress concentration is decreased and not increased, as often happens when the older hardening processes are used.

Illustrative of this, Mr. Benninghoff has stated, in addresses he has delivered, that an engine manufacturer was using an alloy steel crankshaft and, in order to reduce bearing wear, he heat treated it to the limit of machinability. After about 30,000 miles these shafts began to crack. An appraisal of the situation showed that the failures were caused by fatigue due to stress concentration in the fillets. Changing the steel to modified SAE 1050 and Tocco hardening, the failures ceased. Some of these shafts have been running more than 150,000 miles with no perceptible bearing wear.

As to hardness values across a cross section of a hardened part—these are stated to be practically non-variable throughout. The transition from case to core also is what may be termed gradual. There is complete freedom from spalling of the case. There is no free ferrite present but a gradual blending of structures. "The combination of accurate control, split second heating cycles, and pressure quenching applied instantaneously at the end of the heating cycle produces a bond, that is, a cohesion between the hardened area and the core which blends gradually with the core structure without any marked precipitation of free ferrite

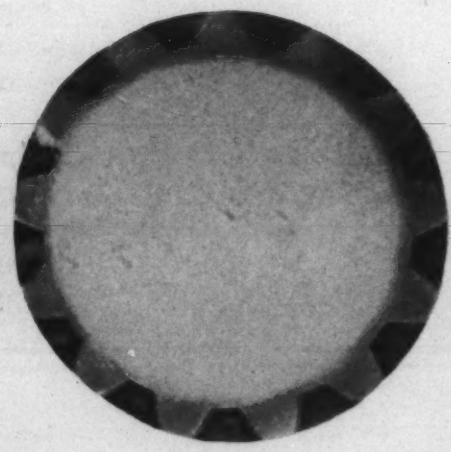
*Tocco Unit for Camshaft Hardening.*



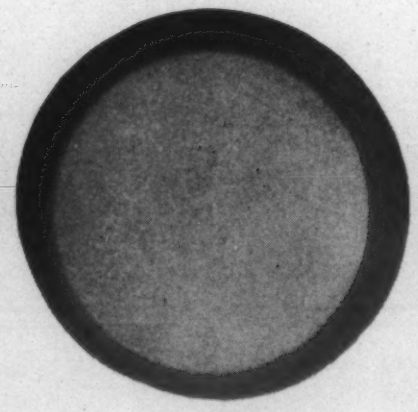


*Automotive Camshafts*

*Steel Cam*



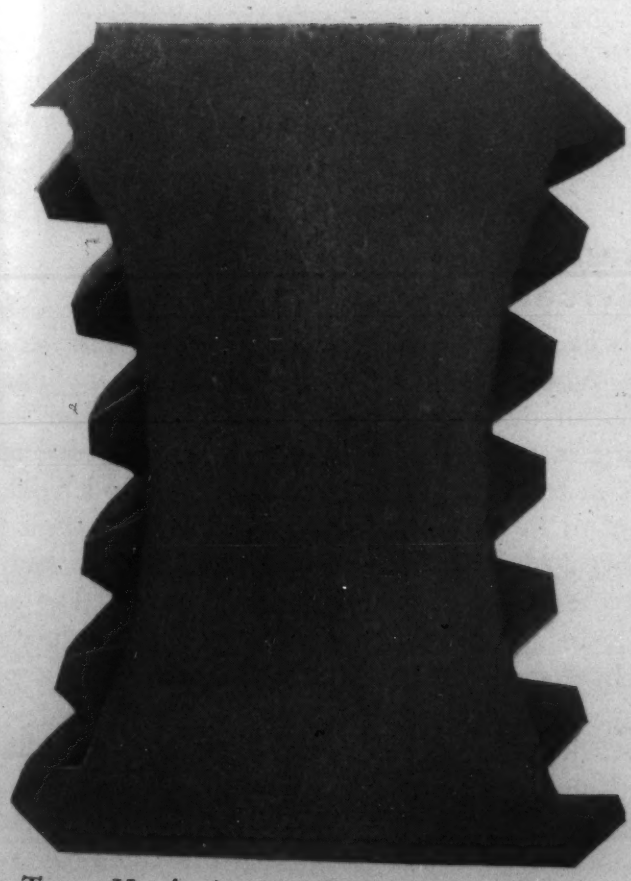
*Steel Gear*



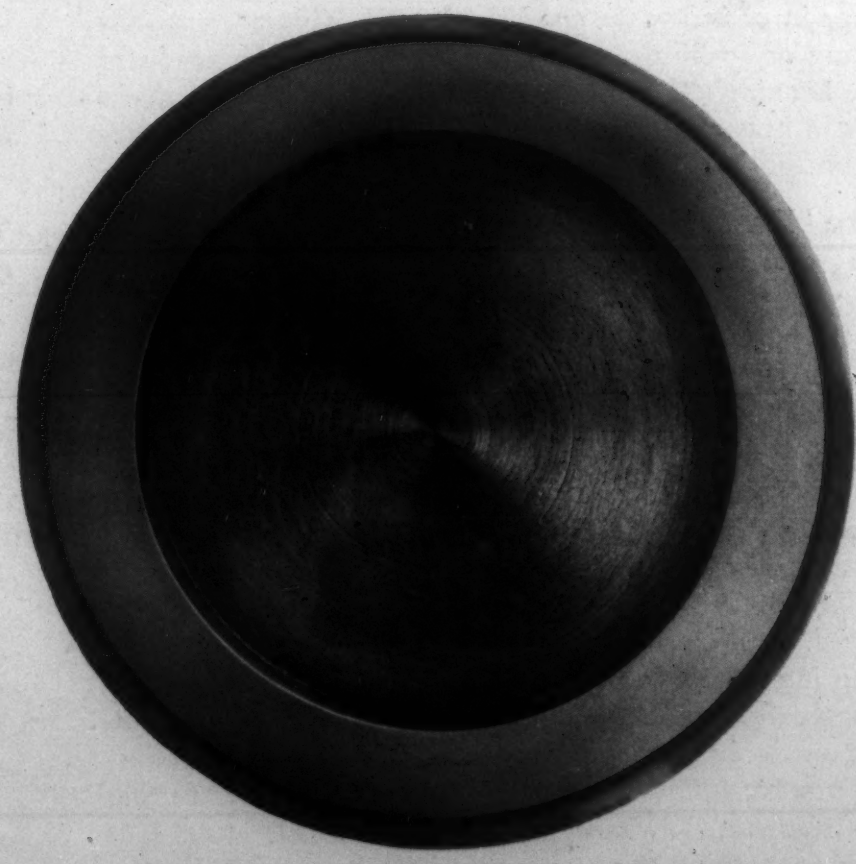
*Eccentric*

*Malleable Cam*

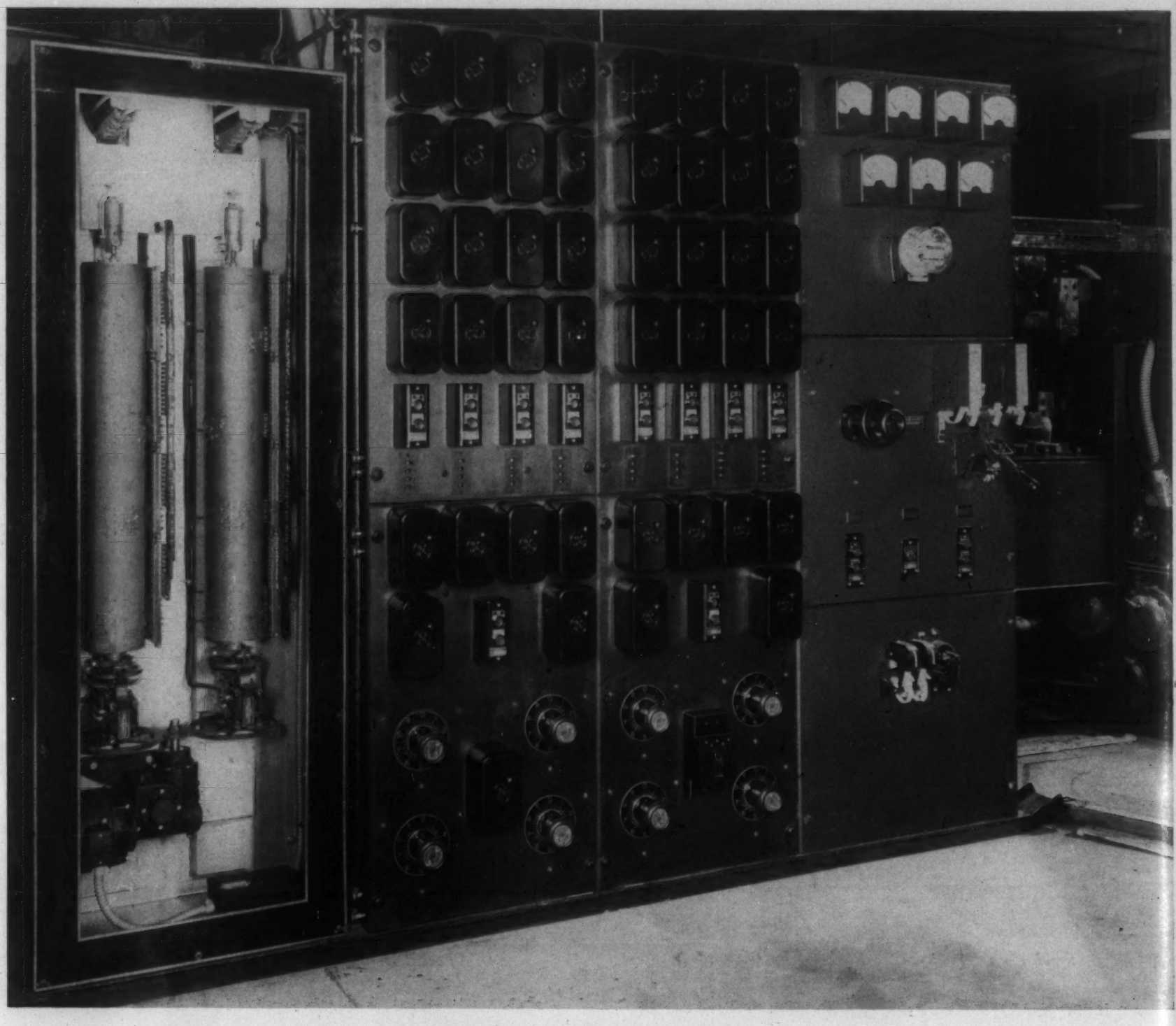
*Typical Camshaft Sections.*



*Tocco Hardening Applied to a Truck Worm.*



*Cross Section of a Tocco Hardened Bearing.*



*Control Board for Vertical Units..*

either in or below the gradation zone." This prevents any flaking or spalling in service. The statement is made by Mr. Benninghoff that out of nearly a half million shafts now in heavy duty service there has not been a single failure in the bond or hardened zone.

## The Bearing Situation

As to the effect of the availability of hard shafts on the bearing situation—undoubtedly harder bearings will be used. But hardness, it is contended, is not an answer to wear—it is structure. New combinations of bearing materials are being investigated and developed. With surface hardened shafts these will permit higher bearing speeds and pressures. And to take advantage of these facts, new engines are being developed. This is pointed out as making possible a consequent increase in horsepower per cubic inch of displacement, or the weight per horsepower can be decreased.

An interesting fact is that, where crankshaft design permits, the forging can be machined in the air quenched instead of the heat-treated state, then hardened by the inductive process followed by finish grinding without further heat treatment—obviously a saving in cost of treating. It is easier to machine the air quenched structure with the saving about 25 per cent of the machining costs and lengthening tool life about 50 per cent. This is pointed to as permitting the use of the hard surface shaft with little or no increase in costs.

## Treating Other Than Cylindrical Shapes

There is keen interest in the question as to whether this hardening process is applicable to other than cylindrical shapes. Camshafts are now being hardened by the Tocco process on a large production scale. There is claimed to be no trouble as to the use of the process for irregular shapes. When applied to camshafts—these are easily machined in the air quenched condition, then the cams, gear and eccentric are hardened and the shaft finish ground. The process can also be applied to axle shafts and similar products such as wheel spindles with the rollers riding directly on the shaft.

As a result of the development of this exceedingly unique and interesting process, it may be said that we now come close to having the ideal crankshaft—one with maximum ductility to withstand physical abuse combined with high bearing hardness so as to withstand wear and abrasion.

## Editorial

*(Continued from page A 15)*

regret that there are now but 6 issues yearly instead of the former 12. The topics are usually a bit high-brow, but the abstracting ordinarily makes them distinctly more readable and intelligible than the originals.

To Louis Jordan, contributing editor of *Mining and Metallurgy,* for his "Previews of Tomorrow's Metallurgy," a monthly feature of that magazine. The "Previews" are well-written, thought-provoking discussions of technical advances in the art and science of metallurgy that make a regular hit with us.

To *Chemische Fabrik,* for the "Dechema Werkstoffblätter" an adjunct to each issue of this semi-monthly publication. The "Werkstoffblätter," edited by Dr. Rabald, present an apparently complete bibliography of published material of international origin on heat and corrosion resistant materials for the chemical industries.

To *Instruments,* for the very instructive series of articles by Professor Williams on "Hardness and its Measurement," which started in the January, 1937, issue and is still running. This is a detailed, comprehensive discussion of a complicated subject given by an acknowledged authority.

To the German investigators (Föppl at the Wöhler Institut and Förster and Köster at the Kaiser-Wilhelm Institut f. Metallforschung) who have so thoroughly probed the mechanism and significance of damping in metals. The work of Föppl was discussed editorially by Dr. Gillett in our December, 1936, issue; recent work by Förster and Köster, published in the April, 1937, issue of *Zeitschrift f. Metallkunde,* explores the relation between damping capacity and other physical properties of both homogeneous and heterogeneous metals. One of their most interesting findings is that not only residual stresses but internal and superficial defects can be detected by measurements of damping capacity.

And finally, to Cyril Wells of Carnegie Institute's Metals Research Laboratory for his illuminating discussion and clarifying investigation of graphitization in highly pure Fe-C alloys, presented at the recent meeting of the American Society for Metals. Dr. Wells sheds new light on many previously controversial points, and settles some of them. He demonstrates effect of nucleation, confirms Kinzel and Moore's evidence of graphitization in very low carbon alloys, proves that graphite forms directly from austenite as well as from carbide decomposition, and that cementite is the unstable form in hypoeutectic Fe-C alloys between 2055 and 1300 deg. F. and possibly down to room temperatures. The discussion is lucid, the logic is rigorous and the micrographs are things of beauty and a joy indeed.—F. P. P.

# A Few Chuckles

### Decrystallization

Those "engineers" and laymen generally that have outraged our metallurgical ears by saying a metal with coarse fracture "has crystallized" have a lonesome counterpart in Britain, who, with a careless abandon that leaves us fearful for the very existence of our industry and profession, makes the bold suggestion that metals are much too crystalline, even normally, and should be drastically modified.

The real danger in the proposal lies in its insidious presentation as a discussion of a metallurgical paper ("The Metallurgical Aspect of the Fourdrinier Wire," H. H. Parrett, *Proc. Tech. Session Paper Makers' Assoc. Great Britain & Ireland,* Vol. 17, Mar. 1937, part 2), for it thus becomes a matter of scientific record much as an apparently innocuous amendment to a Congressional bill is later found to be more destructive economically than the unamended act. Here it is:

"I was particularly interested in Dr. Parrett's explanation of the effect of crystal size and of the relative strength of crystal and binding medium. One is tempted to ask why it is not possible to eliminate crystals altogether and to have only the binding medium present in order to get maximum strength."—F.P.P.

### The Decimal Point

*American Machinist,* Nov. 17, 1937, p. 1093, speaking of the Metal Show, remarks: "Those who inspected the exhibits were 9.944 per cent pure in the genuineness of their interest at least."

We suppose the Machinist's customary measuring to thousandths is responsible for this apparent slur on the purity of those with metallurgical interests.—H. W. G.

### "Brinelling a Molten Metal"

"Small beryllium washers of 14 mm. diameter and 1 mm. thickness by the Brinell test showed a hardness of 70, the same degree as in the compact molten metal."—*Chem. & Met. Eng.,* Dec. 1937, p. 752.

Brinelling a molten metal is new to us. How thick must the molten metal be to avoid the "anvil effect"?—H.W.G.

### Pressure Vessels

Lloyds Register of Shipping publishes requirement for welded pressure vessels *intended for land purposes.*—H.W.G.

# A LETTER TO THE EDITOR

## The Hot Quench for Hardened High Carbon Steel

*To the Editor:* Probably this note will strike a sympathetic chord in some of your readers who are fortunate to have the Rolls Razor.

For many years I have been using one of these finely tempered Sheffield steel blades with its excellent cutting edge. It is a great joy to get up in the morning and know that that old razor is going to do its job just as well as the day before. Not always, however, is this true. Why? Because the manufacturer simply cannot seem to build a satisfactory friction clip, that small insignificant little round spring clip with two tiny ears that places the tension on the blade during stropping. This most innocent looking part that has broken (usually only one of the ears) has too frequently been the flaw in an otherwise perfect day.

Here is a metallurgical problem that suggests the advantages to be obtained from a hot quench. Possibly the makers are not aware of the inherent ductility in the hard constituent "Bainite."

MERRILL A. SCHEIL.

Metallurgical Research,
A. O. Smith Corp.,
Milwaukee.

*Courtesy: Jones & Laughlin Steel Corp.*

*Removing Scale from Sheets and Strip in Pickling Vats*

NOTES ON THE

# Graphitization of Gray Cast Iron

by R. M. Parke, V. A. Crosby and A. J. Herzig

*Research Laboratory, Climax Molybdenum Co., Detroit*

**Abstract:** *The mechanism of the formation of graphite in gray cast iron is discussed and an explanation for the cause of the occurence of a ferritic region (sometimes called "primary ferrite") between a carbidic region and a pearlitic region is proposed.*

CAST IRON IS A COMPLEX iron base alloy of much versatility. Due principally to its high sensitivity to alloy additions and to casting cooling rates, its properties can be modified to meet a variety of uses. Furthermore, its response to heat treatment covers a range that extends from the highest temperature reached in commercial melting practice down to room temperature. Over this range there occurs in cast iron practically every reaction known in metallurgy with the possible exception of the peritectic. It is unfortunate that so little is known of the fundamental physics and chemistry of this valuable material. At the same time it is not surprising that our knowledge of the metallurgy of cast iron is afflicted with an occasional anomaly.

It is proposed to discuss in this paper one such anomaly which concerns the occurrence of a ferritic region between the carbidic (i. e. chilled) region and a pearlitic region in gray cast iron. This condition is often observed in the foundry and has been carefully described by Bancroft & Dierker[1]. Some theories have been advanced to rationalize the phenomenon with our present understanding of the metallurgy of cast iron. Without going into these theories, the present authors submit that the phenomenon will appear reasonable if a certain view of the mechanism of graphitization be assumed, namely—that graphite, in the familiar foundry gray iron, forms normally from the melt.

It is in general believed that in hyper-eutectic cast irons, graphite separates from both the solid and liquid states. However, for hypo-eutectic irons, the belief is generally expressed, especially in this country, that graphite does not form until solidification is complete and then only by decomposition of cementite.

Settlement of this controversial point would be of material advantage to the foundry metallurgist. Further discussion of the subject seems appropriate and the authors, therefore, present below arguments, known to them, in support of and against the belief that hypo-eutectic (as well as hyper-eutectic) gray irons can graphitize before solidification is complete.

## Arguments on the Genesis of Graphite in Gray Cast Iron

THE known rates of graphitization in the solid are not consistent with the amount of graphite appearing in as cast gray iron. Hanemann[2] determined that the time required for graphitization of chilled iron samples of slightly hypo-eutectic composition was 6 hrs. at 1000 deg. C. (1832° F.), the time decreasing with increasing temperature such that, at 1140 deg. C. (2085° F.), the eutectic temperature, it was one hour. Hanemann then presented a photomicrograph of a sample quenched during the solidification period showing graphite growing out into the melt. Hanemann reports that the solidification interval was not over 52 secs., and he concluded that graphite can form from the melt but Epstein[3] comments on the data as follows:

> This would appear to be fairly strong evidence for Hanemann's viewpoint, although it may still be held that the rate of cementite decomposition on cooling from the melt and in the solidification interval may be considerably faster than it is on reheating, even though on reheating the eutectic temperature was reached.

Certainly if we admit that the rate of cementite decomposition in the neighborhood of the eutectic temperature is rapid enough to account for graphitization then we have a right to expect that the graphite shapes will be related to the forms of the primary cementite since the possibility of time for diffusion to assume the familiar random shapes is obviously eliminated.

Bardenheuer[4] has shown instances of a cementite network breaking down to graphite but the relationship be-

tween these graphite forms and the antecedent structure is readily discernible.

Failure to observe kish on a hypo-eutectic iron has been cited as an argument precluding the possibility of graphite formation in the liquid. Sauveur[5] has stated:

> If, on slow cooling, graphite separated directly from molten iron, the bulk of it, at least, should rise to the top of the molten bath and the solidified mass should be found much richer in graphite near its surface than at some distance from it. The author does not understand such heterogeneity in the distribution of graphitic carbon to be observed in the case of gray cast iron castings. To the contrary, on the assumption that graphite results from the breaking up of cementite soon after its solidification, it is readily understood why, in spite of their very great difference in specific gravity, iron and graphite are found uniformly distributed in the various parts of the casting.

From Hanemann's photomicrograph, previously mentioned, and from a similar photomicrograph prepared by Boyles[6] during his excellent research on the freezing of cast iron it seems very probable that graphite and austenite form simultaneously and that the graphite is attached to the austenite and is thus prevented from floating to the top. Concerning his photomicrograph, Boyles makes the following pertinent comment:

> As each flake grows, it forms about itself a layer of solid austenite, which is one of the constituents of the eutectic. Any carbon added to the sides of the flake must diffuse through the layer of solid austenite. Thus, we see that most of the growth must occur at one end of the flake, the end that projects out into the remaining liquid. Under such conditions the growth is dependent upon two factors, —the rate of solidification and the rate at which graphite becomes available.

Much has been written to prove or disprove the existence of an iron-graphite eutectic in addition to the iron-iron carbide eutectic, but it appears that if both eutectics exist the difference between their temperatures is so small that separate identification is extremely difficult.

Examination of the various types of graphite causes one to doubt if graphitization in the solid is sufficient to account for all of them. Graphite produced by malleablizing is known to occur in the solid but the forms assumed by graphite so produced are vastly different from those occurring in gray cast iron. It is difficult to imagine what type of reaction in the solid produced the graphite shown in Figs. 1 and 2. These wandering trail-like forms could conceivably develop only in a random state such as a liquid.

The Symposium on Cast Iron[7] shows that irons in 1½-in. sections and with about 3.50 per cent graphitic carbon, have a volumetric shrinkage during solidification of 0.07 to 0.82 per cent while an iron with 0.56 per cent graphitic carbon shrinks 5.82 per cent during solidification. These data tend to support the idea of graphitization occurring during solidification. Yet Honda and Endo[8] have been reported as concluding that the observed changes in volume are consistent with the view that graphite in cast iron is the result of the decomposition of solid cementite.

Ericson's[9] data on the density changes of cast iron during solidification do not support Honda and Endo's findings and after microscopic examination he stated, "The conclusion drawn now that graphite is actually separated primarily on freezing is thus completely supported by the microstructure."

As a result of carefully controlled quenching experiments, Boyles[6] concluded that pure Fe-C-Si alloys (C 3.49 per cent, Si 2.01 per cent) on solidifying first form long dendrites of austenite:

> These dendrites are the skeletons of crystals, which were never completed because a new mechanism intervened, namely, the freezing of the eutectic. When the melt reached the eutectic temperature solidification began at various centers, which grew equally in all directions, forming masses of spherical shape. Graphite flakes formed immediately upon freezing and continued to grow radially as the spheres developed in size. The result is a rosette of graphite flakes centered about each crystallization point.

This illuminating description of the freezing of cast iron explains, among other things, the mechanism for the formation of the so-called "whorl" graphite.

To confirm further the possibility of the coexistence of graphite and molten cast iron the present authors water-quenched samples held one hour at successively higher temperatures and examined the microstructure. The iron was of the following analysis: T.C. 3.39, C.C. 0.52, G.C. 2.87, Si 2.29, Mn 0.88, S 0.087 and P 0.183 per cent.

It was found that at 2010 deg. F. the sample was partially molten and that in the central portion flake graphite existed, but at 2025 deg. F. the sample was completely molten and flake graphite had entirely disappeared (Fig. 3). To ensure that a stable equilibrium had been established another sample was held 2 hrs. at 2010 deg. F. and then quenched. This sample had been partially molten but microscopic examination revealed that the flake graphite persisted (Fig. 4).

## Proposed Explanation of the Cause of the Occurrence of a Ferritic Region Between a Carbidic and a Pearlitic Region in Cast Iron

WITHOUT concluding at this time that a hypo-eutectic iron can graphitize from the melt, let it be assumed that this is the case. On this basis it can be shown how a ferritic-graphitic region can occur between the chilled (white) and pearlitic-graphitic regions in cast iron.

If a cast iron is of such composition and has been subjected to a cooling rate such that the microstructure is predominantly pearlite and flake graphite, we may conclude that very little graphitization took place in the solid state. During solidification sufficient graphite separated from the melt to change the composition of the matrix to approximately that of eutectoid composition.

If, however, the cooling rate of this same iron is increased considerably, due to insufficient time for formation of the usual amount of graphite in the liquid, some primary cementite will be formed along with the austenite highly saturated with respect to carbon. The saturated austenite and primary cementite, both being highly unstable, will have a tendency to graphitize, and on passing through the critical will form ferrite. Because of the high degree of supersaturation of the austenite, a large number of graphite nuclei will appear and because of the low rate of diffusion of carbon in the solid state the particles will remain small.

*Fig. 1. Etched in 2 Per Cent Nital. 500 X.*

Graphite so formed is not readily confused with the large flakes formed during slow solidification.

If the cooling rate of this iron is very slow (especially during the $\gamma$ to $\alpha$ transformation) then there is the possibility of graphitizing the pearlite and again producing ferrite, even though the normal amount of graphite was formed during solidification.

*Fig. 2. Etched in 2 Per Cent Nital. 500 X.*

We may say then that this cast iron has four principal cooling rate ranges:

1. A rapid cooling rate such that graphite is formed neither in the liquid nor the solid state, producing a chilled or white iron.
2. A less rapid rate, especially after solidification is complete, such that little or no graphitization takes place

*Fig. 3. Etched in 2 Per Cent Nital. 500 X.*

*Fig. 4. Etched in 2 Per Cent Nital. 500 X.*

*Fig. 5. As Cast-Chilled Region. Etched in 2 Per Cent Nital 500 X. Analysis: 3.67 C, 2.64 Si, 0.28 P, and 0.06 Per Cent S.*

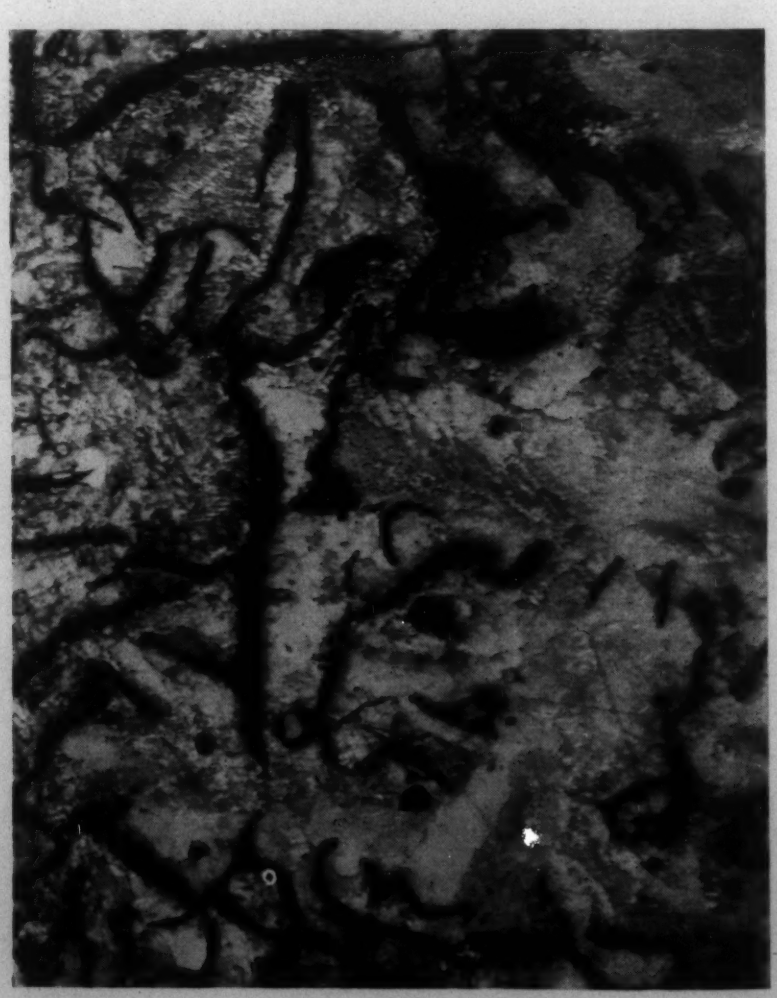
*Fig. 6. As Cast-Chilled Region. Etched in 2 Per Cent Nital. 500 X. Analysis: 2.94 C, 2.58 Si, 0.012 P, and 0.043 Per Cent S.*

in the melt but the unstable saturated austenite or cementite does have time to graphitize in the solid, thus forming the so-called "primary ferrite" on reaching the critical temperature.

3. A still slower rate, such that graphite is formed in the melt in quantities sufficient to form an all pearlitic matrix.
4. An extremely slow rate where graphitization occurs in both the solid and liquid states, producing a graphitic-pearlitic-ferritic structure.

*Fig. 7. As Cast-Pearlitic Region. Etched in 2 Per Cent Nital. 500 X. Analysis: 3.67 C, 2.64 Si, 0.28 P and 0.06 Per Cent S.*

*Fig. 8. As Cast-Pearlitic Region. Etched in 2 Per Cent Nital. 500 X. Analysis: 2.94 C, 2.58 Si, 0.012 P and 0.043 Per Cent S.*



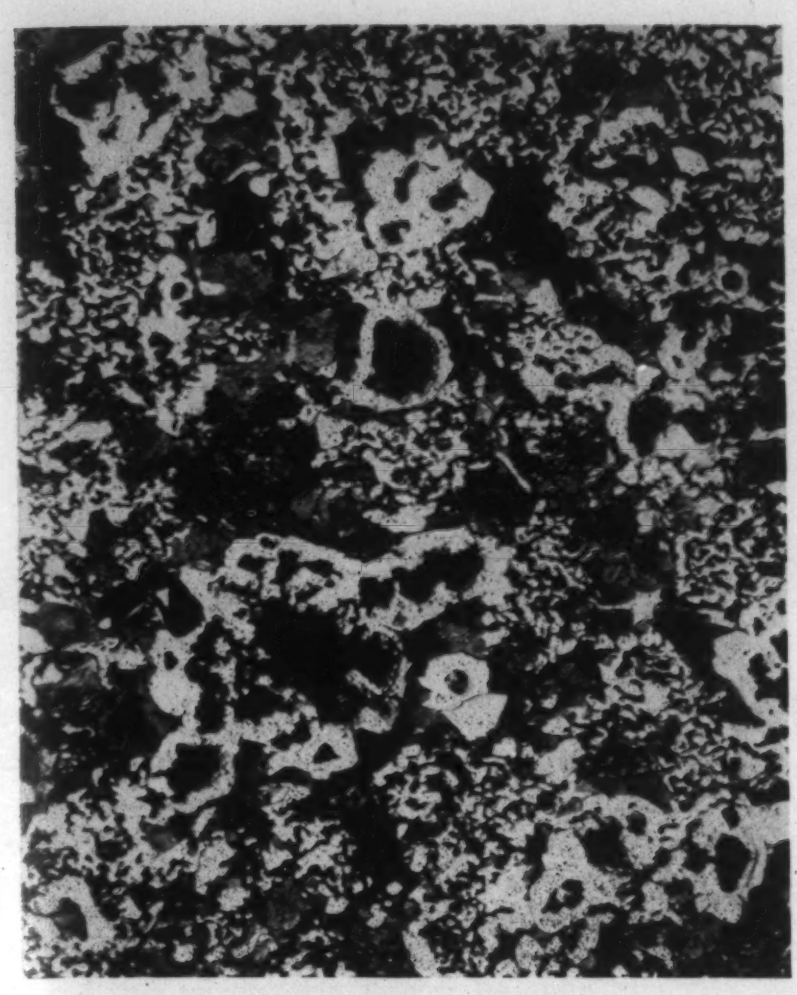


*Fig. 9. As Cast-Ferritic Region. Etched in 2 Per Cent Nital. 500 X. Analysis: 3.67 C, 2.64 Si, 0.28 P and 0.06 Per Cent S.*

*Fig. 10. As Cast-Ferritic Region. Etched in 2 Per Cent Nital. 500 X. Analysis: 2.94 C, 2.58 Si, 0.012 P and 0.043 Per Cent S.*

The study of the formation of "primary ferrite" may be conveniently performed on thin wedges, about ¼ in. thick at one end, 1/32 in. thick at the other, and 5 in. long. The shape of this specimen is such as to provide a wide range of cooling rates. A number of these wedge shaped samples were cast first using a slightly hyper-eutectic iron of 3.67

*Fig. 11. Heat-Treated Chilled Iron. Etched in 2 Per Cent Nital. 500 X. Analysis: 3.67 C, 2.64 Si, 0.28 P and 0.06 Per Cent S.*

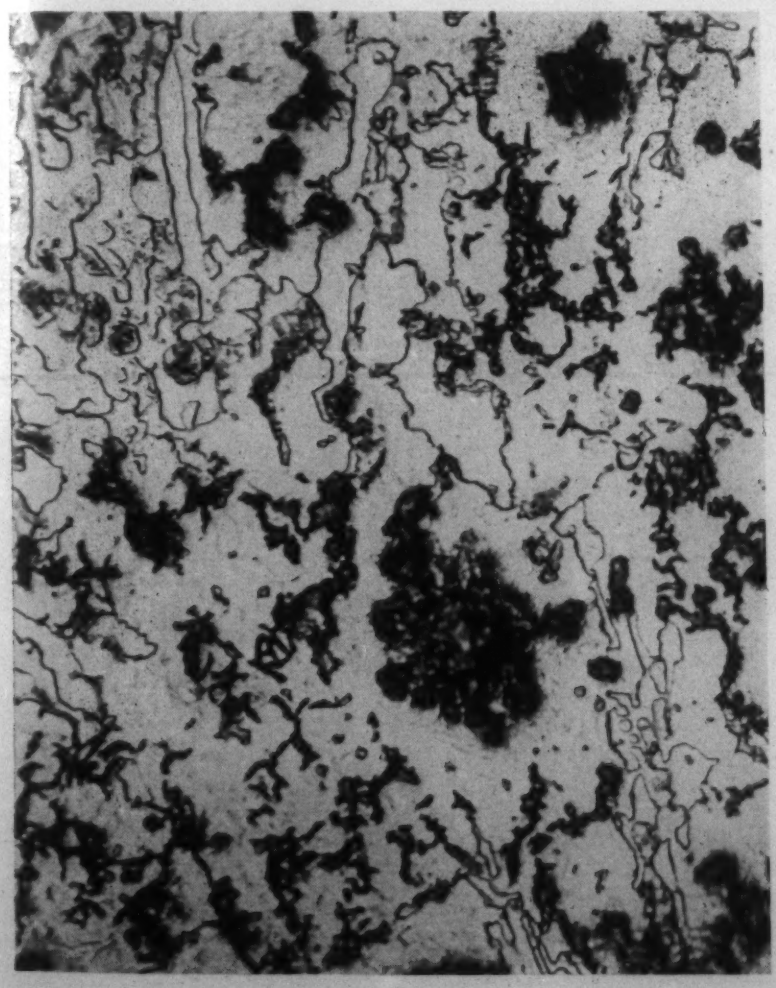
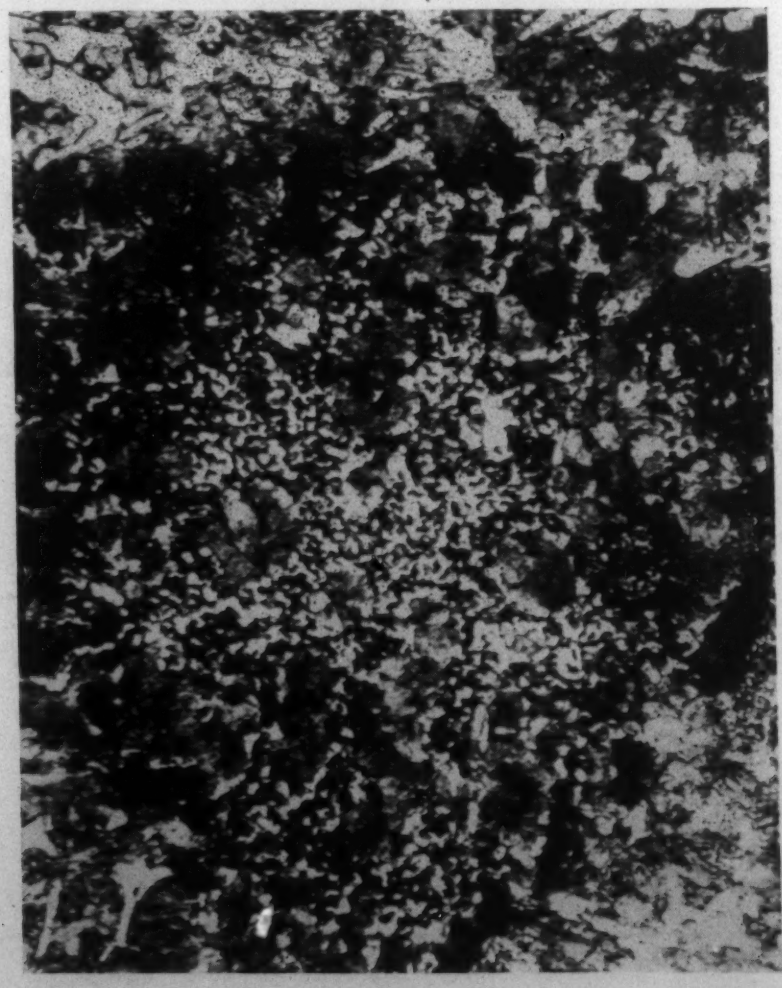


*Fig. 12. Heat-Treated Chilled Iron. Etched in 2 Per Cent Nital. 500 X. Analysis: 2.94 C, 2.58 Si, 0.012 P and 0.043 Per Cent S.*



C, 2.64 Si, 0.28 P, 0.06 per cent S, and then using a hypo-eutectic iron of 2.94 C, 2.58 Si, 0.012 P, 0.043 per cent S. At the points of the wedges of each iron the typical structures of chilled iron are found. These structures are shown in Figs. 5 and 6. At the other ends of the wedges a graphite pearlite structure is found as shown in Figs. 7 and 8. The intervening structures are shown in Figs. 9 and 10.

The graphitization has not proceeded as far in the intermediate zone of the hypo-eutectic iron as it has in the hyper-eutectic iron. In addition it was found that a fine graphite having the denritic pattern was more likely to occur in the case of the hypo-eutectic iron than in the hyper-eutectic iron. The hypo-eutectic iron being somewhat further removed from eutectic composition than the hyper-eutectic iron, probably reached the eutectic temperature with a smaller percentage of liquid of eutectic composition, so that when graphitization began its sphere of operation was necessarily restricted to the interstices of the austenite dendrites. The graphite in the intermediate zones is noticeably different from that in the heavier sections.

Although a macro-etch of the wedge reveals a very sharp line of demarcation between the chilled and gray sections, if one examines the wedge at a magnification of 1500 diameters one will note that on traveling away from the chilled end the amount of graphite gradually increases, while the amount of carbide decreases, and the amount of pearlite and ferrite increases up to the center of the intermediate zone containing "primary ferrite." Going from the center of the intermediate zone to the heavier section, it will be noticed that the amount of ferrite decreases, while the amount of pearlite increases. In the boundary between the chilled zone and the zone of "primary ferrite" cementite disappears entirely.

If the wedges are heated at 1700 deg. F. for 2 mins., then placed in a furnace at 1000 deg. F. for 5 mins. (the latter temperature permitting a slow cool through the critical to avoid formation of martensite) it will be found that "primary ferrite" will be produced in the "austenitic" needles of the chilled sections. Figs. 11 and 12 show the microstructure of the chilled sections after the above heat treatment. Note the similarity of the graphite-ferrite "rosettes" to those in Figs. 9 and 10.

The mechanism of the formation of the two types of graphite found in the wedge may be described as follows:

1. The graphite in the pearlitic-graphitic (i. e. largest) section formed before solidification was completed.
2. The graphite in the "primary ferrite" section formed by precipitation from the solid state. This section was "white" immediately upon solidification but the adjacent heavier section sufficiently retarded the cooling rate to permit graphitization to occur down to the critical range where ferrite and more graphite were produced.

## Conclusion

An explanation of the anomalous occurrence of ferrite adjacent to a chilled section in cast iron may be evolved if one adopts the view that graphite can form in both the liquid and the solid state.

In the opinion of the authors, this explanation may be considered as additional evidence for the belief that all the usual foundry gray cast irons can graphitize just before solidification is complete.

Such a belief is further supported by its ability to explain a) the cause of the difference between the shapes of graphite in gray cast iron and those in malleable iron, b) the mechanism of the formation of whorl graphite, c) the density changes of cast iron during solidification, d) the rapid graphite formation in gray cast iron as compared with the slow rate of graphite formation during the malleablization of white iron.

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## SOME HELPFUL ACCESSORIES IN

# Practical Spectrographic Analysis


## by J. S. Owens

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SPECTROCHEMICAL TECHNIQUES have been developed at The Dow Chemical Co., to serve many of the analytical needs of a diversified chemical and metallurgical manufacturing plant. Appropriate analytical spectral sources and methods are used for the analyses of the different materials to obtain maximum sensitivity, rapidity, and accuracy. These factors constitute the principal advantages of spectrochemical analysis. Interesting results in the purification of graphite rods for use as spectroscopic electrode supports have been obtained by the use of high temperature, electric heating in vacuum. The spectral sources used include condensed sparks, alternating[1] and direct current arcs, and the cathode layer of the direct current arc.[2] The quantitative analytical methods use internal standard elements,[3] intensity calibration of each plate by the Hansen step-diaphragm,[4] and graphical conversion of microphotometer readings into percentage concentrations. Several thousand quantitative analyses are ordinarily made each month.

*Fig. 1. Alignment Pointer for the Spectral Source.*

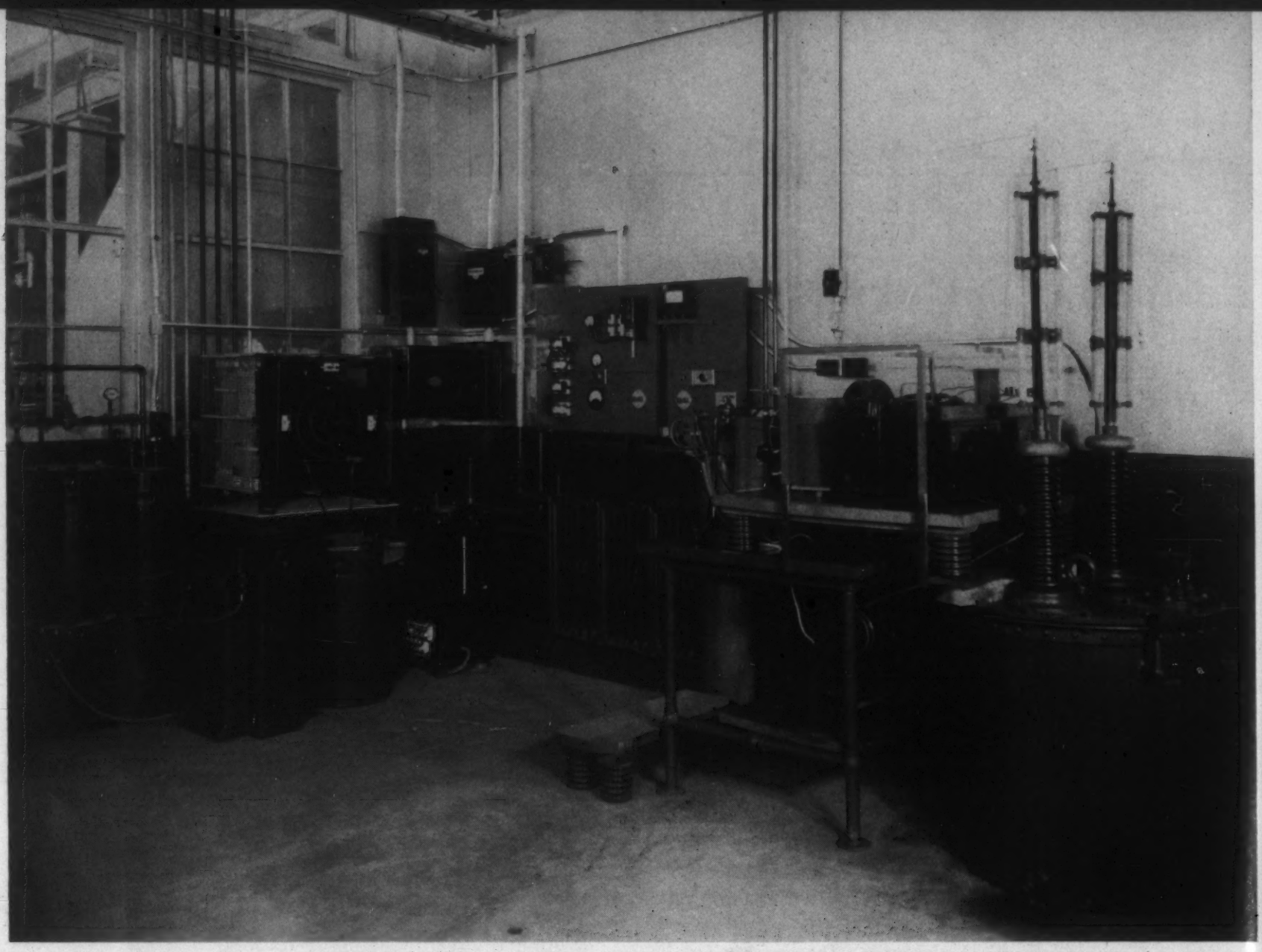


*Fig. 2. Spectroscopic Source Equipment for the Production of the Condensed Sparks, the D. C. Arc, and the A. C. Arc*

## Purification of Graphite Electrodes

Commercial graphite of spectroscopic quality contains appreciable amounts of iron, silicon, boron, magnesium, calcium, aluminum, copper, titanium, and vanadium. Although graphite containing considerably smaller amounts of these materials can be obtained, its purity is not completely satisfactory and its cost is considerable. Since the use of impure graphite electrodes introduces a probable source of error in the analysis of many materials, several methods of purification have been developed.[5]

The method of purification developed in this laboratory possesses the advantages of simplicity and efficiency. It comprises high temperature heating of the graphite in an evacuated furnace. The temperature of the graphite is measured with an optical pyrometer.

Tests of the effects of variations, in temperature and in time of heating and of the use of different degrees of vacuum and different gases as a medium surrounding the graphite have led to the following conclusions:

1. Treatment at temperatures below 2000 deg. C. is ineffective.
2. The purity obtained increases with increasing temperature up to 2460 deg. C., the maximum temperature possible with the present apparatus.
3. The purity obtained by treatment, at a constant temperature, in air at a pressure of 6 in. of mercury is intermediate between that at a pressure of less than 1 in. of mercury and that at atmospheric pressure.
4. Treatment at atmospheric pressure in air, nitrogen, helium, or hydrogen is, in general, somewhat less effective than in vacuum. The purity obtained in air is practically the same as that obtained in nitrogen, or helium, but slightly greater than that obtained in hydrogen.
5. The preferred method of purification consists of heating at temperatures of 2460 deg. C., or higher in an evacuated furnace.

Graphite of greater purity than that of the best spectroscopic graphite previously commercially available can be produced by this method.

This method of purification removes from the commercial graphite rods of spectroscopic quality calcium, copper, aluminum, titanium and vanadium completely, and all but occasional very slight traces of iron and silicon, but does not remove boron. Graphite so treated contains less iron, silicon, calcium, and copper, but more boron than the purest commercial product. Neither contains aluminum, titanium, or vanadium.

Graphite rods purified by this method may be used with safety as electrode supports for the analyses of materials for any element except carbon and boron, even when sources of the high sensitivity possessed by the A. C. arc and the cathode layer of the D. C. arc are used.

## Spectral Source Alignment Pointer

The diversity of the analyses carried out in this laboratory each day requires the use of different types of electrode holders and of different locations of the spectral sources. This prevents the use of fixed holders in which the electrodes are in constant alignment. In order to conserve time and to insure accuracy in the alignment of the source the pointer shown in Fig. 1 was developed. In one operation by its use the source is located at the de-

sired distance from the spectrograph slit, and is aligned vertically and horizontally, and the electrodes are properly spaced. Fig. 1 shows also the brass, spring-action holders designed for use with alloy electrodes.

## Arc Spectral Sources

In order to maintain high analytical efficiency considerable effort has been devoted to the development and refinement of spectral sources most suitable for the analyses of different types of materials. Sources now in use consist of condensed sparks powered by 1 kva, 25,000-volt and 10 kva, 50,000-volt transformers, the D. C. arc, the cathode layer of the D. C. arc, and the A. C. arc. Fig. 2 shows the equipment for all four of these sources set up in a compact switchboard controlled form. The right-hand portion of the figure shows the condensed spark equipment, controlled by the corresponding part of the switchboard. The left-hand portion shows the A. C. arc equipment, controlled by the corresponding part of the switchboard. The plug and controlling switch for the 300 volt supply for the D. C. arc are seen mounted on the wall directly to the right of the switchboard.

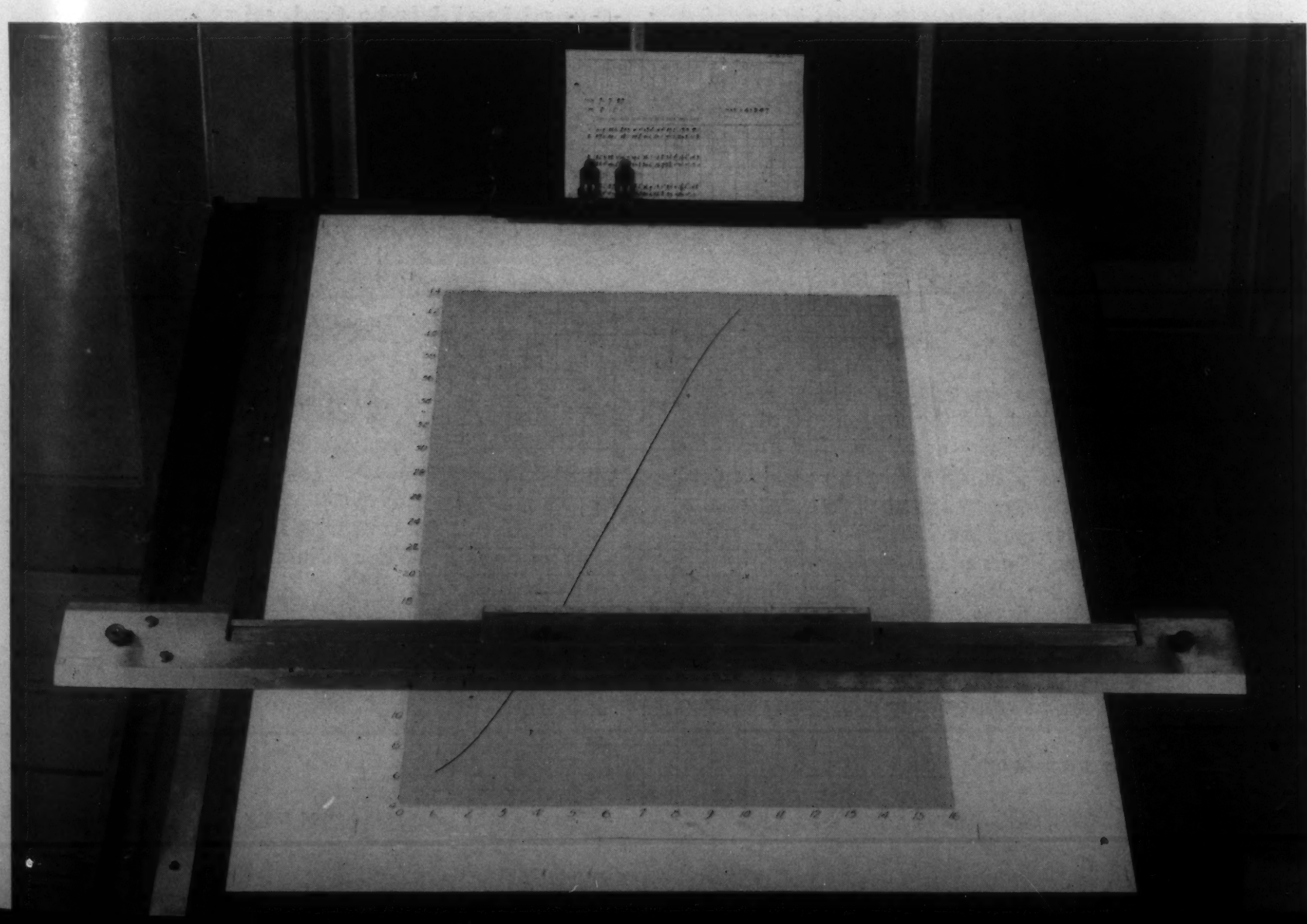
By switchboard control of the A. C. arc equipment either of the transformers shown may be used as the arc transformer and the other may be used as a variable secondary impedance in series with the arc gap to control the arc current or may be entirely removed from the circuit. A variable, iron-core inductance in the primary circuit controls the maintenance of the arc by controlling the voltage-current phase relationship. With the alternating current supply available some primary inductance is required under most experimental conditions for the maintenance of the arc. This equipment permits the use of secondary voltages of 1100, 2200, or 4400 volts and of continuous arc currents from 2 to 10 amps.

The applicability for analytical purposes of the A. C. arc has been demonstrated by Prof. O. S. Duffendack and his co-workers at the University of Michigan.[1] The advantages of this spectral source, as found both in their laboratory[6] and in this one, make it appear to be of great industrial importance for the analyses of chemical materials. These advantages include ease of maintenance, ease of control of excitation conditions, high sensitivity, low background density and accuracy. By proper choice of the primary inductance critical conditions for the maintenance of the arc can be obtained for almost any normal arc current and for any electrode material. The amount of primary inductance required for such critical conditions, for any one electrode material at a constant electrode separation, is roughly inversely proportional to the arc current. Thus, under certain restricted conditions, circuit constants may be chosen for which the arc will maintain only until the salt under analysis is completely volatilized. Under these conditions the excitation of the spectra of the metallic impurities in a graphite electrode support may be well inhibited. However, at arc currents greater than three amperes, such conditions are difficult to obtain with a stable arc. Since the spectral sensitivity increases with the arc current, the use of specially pure graphite electrode supports is often preferable to the use of such critical conditions.

The electrode holders are preferably water cooled because the background density is considerably reduced, while the sensitivity is but slightly decreased, thereby.

A comparison of the spectral sensitivities of detection of impurities present as traces in some representative chemical materials by different analytical sources gave the following results. The sensitivities of detection in the A. C. arc and cathode layer sources of iron, silicon, manganese, calcium, aluminum, strontium and copper in sodium hy-

*Fig. 3. Graphical Plate Calculator. The ordinate represents "Blackening"; the abscissa is the "Logarithm of Intensity."*



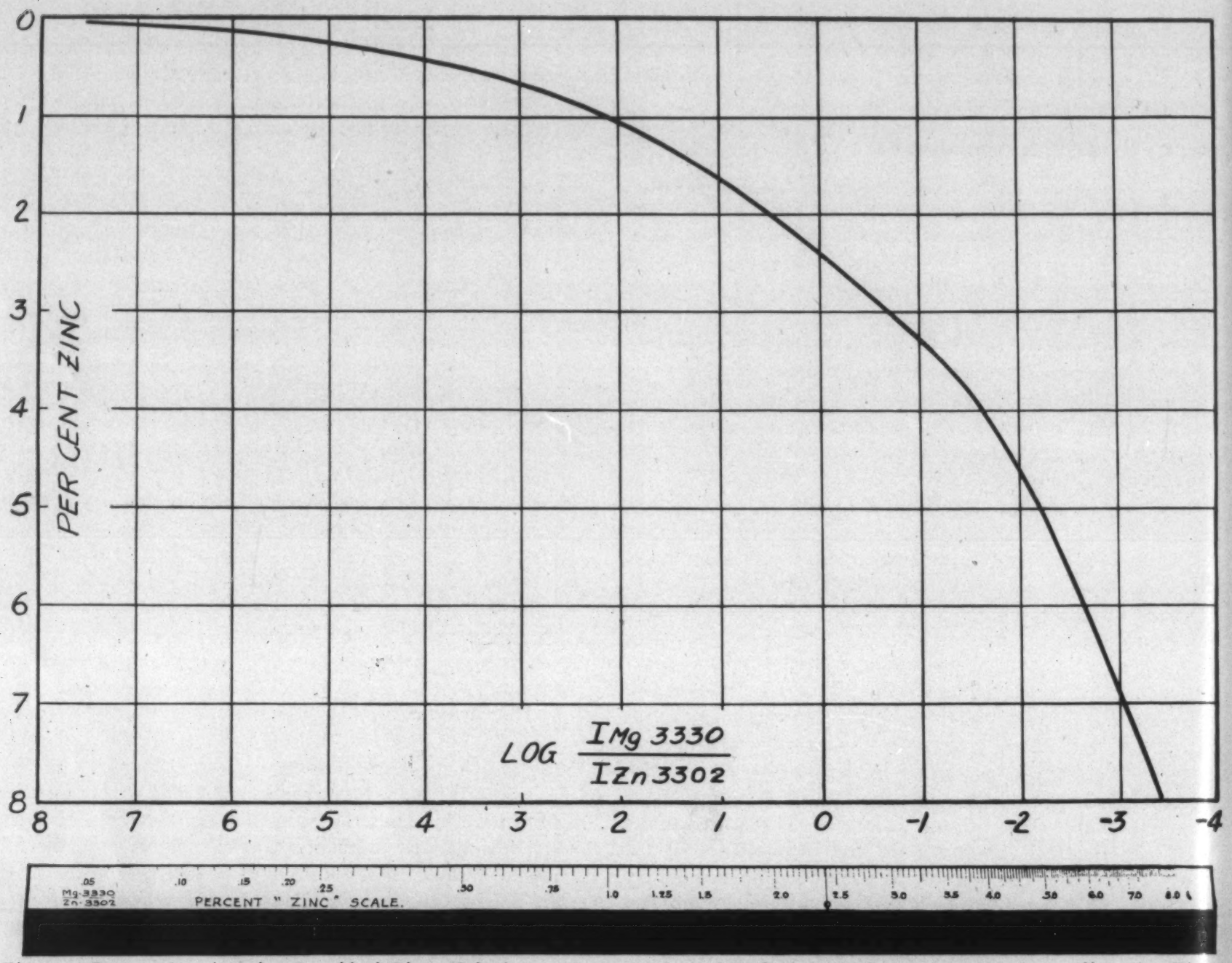



*Fig. 4. Preparation for the Graphical Plate Calculator of an Analytical Scale for Analysis of Magnesium Alloys for Zinc.*

droxide are comparable, that in the D. C. arc is somewhat less. The sensitivity of detection of vanadium in sodium hydroxide is comparable in the A. C. arc and the cathode layer, but is five-fold lower in the D. C. arc. The sensitivity of detection of phosphorus in sodium acid phosphate solutions and of silver in sodium chloride solutions is from five to ten-fold greater in the A. C. arc than in the cathode layer and the D. C. arc. In the spectra of all of these materials the background density is much lower in the A. C. arc than in the other sources. In general, the sensitivity of detection in the A. C. arc of any metallic constituent of a chemical material is of the order of magnitude of 0.0001 per cent.

Upon the basis of these representative analyses and of others, it is concluded that for the analysis of many industrial chemicals the sensitivity of the A. C. arc is comparable with, or greater than, that of the cathode layer, while that of either is, in general, greater than that of the whole D. C. arc. However, neither the A. C. arc nor the cathode layer shows, in general, a greater sensitivity for the analysis of solid alloy electrodes than does the D. C. arc. The advantages of the A. C. arc over the cathode layer for quantitative analysis consist of much weaker background radiation, the uniformity of line intensity throughout the entire usual arc length, and the elimination of any optical system for accurately focussing a restricted portion of the arc upon the spectrograph slit.

## Graphical Plate Calculator

This instrument was developed in order to increase the speed of quantitative analysis in which an internal standard element is used by reducing to a single, graphical step the conversion of spectral line blackenings, obtained with a microphotometer, into percentage concentration of the element under analysis. The chief advantages of the apparatus lie in the economy of time and the decreased probability of arithmetical error. Both are achieved by the great simplification in the arithmetical portion of the conversion.

*Plan of Apparatus:*

The calculator proper, illustrated in Fig. 3, consists of a drawing board equipped with a duralumin parallel straight edge attachment constrained to move only in a direction perpendicular to its length. Lengthwise motion of the straight edge is prevented by radial ball bearings, bolted to its under side, which run in a steel roller track mounted on the board in the direction of the desired motion of the straight edge. An analytical scale is made from the analytical curve for the analysis of the material for each element by projecting the ordinates in percentage concentration of A upon the abscissae in $\log \frac{I_S}{I_A}$, the logarithm of

the relative intensity of the comparison spectral line pair, where S is the internal standard element and A is the element under analysis.

Fig. 4 shows the preparation of an analytical scale for the analysis of magnesium alloys for zinc. The original "zero value" of the $\log \frac{I_S}{I_A}$ units is retained at its proper place upon the scale. The resulting analytical scales are inked in on Bristol board and attached with clear lacquer to duralumin scales one foot long. These duralumin scales make a sliding fit on the parallel straight edge, are capable of motion along its length, and may be clamped tightly to it at any point.

*Method of Use:*

The blackenings* of the spectral lines and of the steps of the intensity calibration pattern obtained by the use of the Hansen step-diaphragm[4] are measured with a microphotometer. The characteristic curve of the photographic plate is obtained by plotting the blackenings of the steps of this pattern against the logarithms of the corresponding light intensities. The characteristic curve is drawn upon cross-section paper which is then fastened to the drawing board as shown in Fig. 3.

* Blackening as used in this paper is defined as the difference between the galvanometer deflection of the micro-photometer for the spectral line (or for the step of the intensity calibration pattern) and the deflection for the clear photographic plate.

The appropriate analytical scale for the element under analysis is placed upon the straight edge. The straight edge and scale are moved until the "zero" of the $\log \frac{I_S}{I_A}$, retained on the scale, intersects the characteristic curve at the blackening of the selected spectral line of S. The scale is clamped to the straight edge and the latter is moved until the scale intersects the characteristic curve at the blackening of the selected spectral line of A. The value read from the analytical scale at this point of intersection gives the percentage concentration of A, the element under analysis.

The complete analysis of the specimen is made by repeating this procedure with the analytical scales appropriate for the analyses for the different elements under test.

If desired, all the analytical scales for the analysis of one type of material for several elements could be mounted on one wide, duralumin bar, with preferably all the $\log \frac{I_S}{I_A}$ "zero values" lying in a straight line perpendicular to the edge of the bar. The different analyses could then be made by means of a sliding, hairline index, similar to that used on a slide rule.

Continuous use of this apparatus in routine production control analyses of magnesium alloys has shown that this graphical conversion of microphotometer readings into percentage concentrations:

1. Is at least twice as rapid as arithmetical conversion.
2. Yields an analytical precision equal to that of arithmetical conversion.
3. Decreases the probability of arithmetical error.

## Summary

Descriptions are given of four useful accessories for practical spectrochemical analysis.

1. Purification of graphite electrodes by high temperature, electrical heating in vacuum.
2. Alignment pointer for the spectral source.
3. A. C. arc spectral source.
4. Graphical plate calculator for the conversion of microphotometer readings into percentage concentrations.

The use of this special equipment and technique has increased the sensitivity, rapidity, and accuracy of the analyses of metallurgical and chemical materials.

## Acknowledgment

The writer wishes to express his appreciation to The Dow Chemical Co., for permission to publish this work. He is also indebted to the members of the X-ray and spectroscopy department for their cooperation in this investigation, particularly Dr. J. D. Hanawalt, director, Dr. J. S. Peake, and R. G. Fowler. The latter took an active part in the experimental work.

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*Pouring a Large Iron Casting in an American Foundry*

A CORRELATED ABSTRACT ON

# Corrosion and Corrosion-Resistant

## METALS AND ALLOYS


## by V. V. Kendall

*Section Editor, Current Metallurgical Abstracts of* METALS AND ALLOYS


*This is another in a series of abstracts by the author relating to symposiums on corrosion problems. The first was published in* METALS AND ALLOYS *for November and covered ferrous materials. The second—on non-ferrous metals and alloys—appeared in the December issue. This one covers the A. S. T. M. Symposium on Corrosion Testing in 1937. The scope of the symposiums abstracted in the first two articles was outlined in the first installment.*

ALONG WITH THE DEVELOPMENT of new metals and alloys for resisting the increasingly severe demands of modern service conditions, the question of corrosion testing has come in for its share of attention. It is necessary, before trying out a new metal or alloy for a particular service condition, to have at least a fairly accurate idea as to whether that metal or alloy will resist satisfactorily the conditions to which it is to be subjected. Corrosion tests have been devised, some for general information and others, for specific information. A quite voluminous literature and much controversy have resulted. In an effort to survey the present status of corrosion testing, particularly with the possibility in mind of standardizing such tests as seemed capable of standardization, the American Society for Testing Materials held a "Symposium on Corrosion Testing Procedure" in March, 1937. [A list of the papers at this symposium is given in the references at the end of this section.—Editor]

A comprehensive review of the factors influencing the rate of corrosion and their application to corrosion testing was given by Borgmann and Mears[50]. As a result of their survey they concluded that sufficient data were available for standardizing the following tests:

A. Laboratory tests:
   1. Impingement attack.
   2. Intercrystalline corrosion.
      a. Stainless steel—immersion in solution of sulphuric acid plus copper or ferric sulphate.
      b. Duralumin alloys—alternate immersion in a solution of sodium chloride plus hydrogen peroxide.
   3. Frequency of sites of initial attack.
   4. Corrosion-fatigue.
   5. Partial immersion tests.
   6. Spray tests.

B. Field tests:
   1. Atmospheric exposure tests.
   2. Soil corrosion tests.
   3. Immersion tests.

They did not recommend the standardization of the following:

Laboratory tests:
   1. Stress corrosion.
   2. Film breakdown tests.
   3. Bimetallic (galvanic) corrosion.
   4. Crevice tests—shielding.
   5. Total immersion tests.
   6. Alternate immersion tests.
   7. Dezincification of brass.
   8. Soil corrosion.

As McKay and LaQue[53] point out, for certain purposes such as control of material and comparison of results on similar materials by different laboratories, standardization is both possible and advisable. For theoretical investigation or original research, it is neither possible nor advisable. However, they bring out very strikingly the necessity of controlling conditions in corrosion testing. In a survey of corrosion tests, reported in the literature over the last ten years, to determine the extent of control and completeness of records in corrosion testing, they reviewed 62 papers, of which 43 were laboratory tests (23 from 1925 to 1929, and 20 from 1930 to 1935) and 22 were field tests (7 from 1925 to 1929 and 15 from 1930 to 1935). Three papers referred to both types of test. The analysis was made considering in one case both types of test, and in another only the laboratory tests. The exclusion of the field tests did not change the results significantly and consequently all tests were included in the analysis as given in Table VI.

> The conclusions to be drawn from these rough figures can hardly be considered immutable but are none the less interesting. It is seen that considering all the various items, the tendency is almost universally toward better control and more complete reporting. The only notable exception to this is the case of solution composition, which seems to have been less completely controlled in the latter tests. This is

**Table VI—Analysis of Some Reports on Corrosion Tests Appearing in the American Literature from 1925-1935**

| Item | Percentage of Reports in Which Various Items Were Described, Controlled or Reported: Period 1925 to 1929 Per cent | Period 1930 to 1935 Per cent |
|---|---|---|
| Description of Test Procedure: | | |
| Specimens | 76 | 91 |
| Testing apparatus | 90 | 91 |
| Composition of materials tested | 66 | 82 |
| Preparation of specimens | 69 | 85 |
| Method of support of specimens | 66 | 94 |
| Duration of test | 93 | 100 |
| Method of cleaning specimens after test | 59 | 57 |
| Control of Corrosion Factors | | |
| Composition of solution | 83 | 70 |
| Temperature | 52 | 69 |
| Aeration | 38 | 40 |
| Velocity | 33 | 52 |
| Change of corrosion rate with time | 50 | 44 |
| Evaluation of Results: | | |
| By weight loss | 76 | 76 |
| By pitting measurements | 10 | 17 |
| By physical tests | 10 | 21 |

probably due to an increased percentage of field tests in the later years in which the composition of the solution is taken as it exists and not subjected to control by the investigator. Approximately 90 per cent or over of the tests since 1930 have described the specimens, the apparatus, the method of support, and the duration. These items, therefore, may be considered as adequately taken care of in the average corrosion test and thus may not need outside instructions.

The percentage taking cognizance of the composition of material, preparation of specimens, composition of solution, run from 80 to 90 per cent, and these items, therefore, seem capable of more improvement than is now taking place.

The evaluation of the results and the units used to report them, as listed in Table VII seems to be quite non-uniform.

**Table VII—Units Used for Reporting Corrosion Rates**

| Units | Number of Papers: Period 1925 to 1929 | Period 1930 to 1935 |
|---|---|---|
| Mg. per Sq. Dm. per Day | 2 | 5 |
| Mg. per Sq. Cm. per Day | 4 | 3 |
| Penetration in Cm. per Year | 2 | 2 |
| Volume of Hydrogen Evolved | 3 | 0 |
| Penetration in Inches per Month | 1 | 2 |
| Mg. per Sq. Cm. per Year | 1 | 1 |
| Grams per Sq. Cm. per Day | 1 | 1 |
| Grams per Sq. Cm. per Test Period | 1 | 0 |
| Mg. per Sq. Cm. per Month | 1 | 0 |
| Ounces per Sq. Ft. per Year | 0 | 1 |
| Per Cent Weight Loss | 1 | 0 |
| Mg. per Sq. Inch per Test Period | 0 | 1 |
| Penetration in Inches per Day | 0 | 1 |
| Penetration in Cm. per Day | 0 | 1 |
| Consumption of Oxygen per Sq. Dm. per Min. | 0 | 1 |

Note: In the other papers analyzed no numerical units were used.

This is possibly logical because the detailed purpose of the tests varies considerably from test to test. In spite of this, the writers believe that a certain improvement in the direction of uniformity might be made by well-considered procedure.

This leaves three important features of the method of making tests which definitely and positively affect the rate of corrosion and which are covered in only about 50 per cent of the tests being made today. This is in spite of the fact that these factors have been repeatedly shown, in well-conducted experiments to have controlling effects. These three factors are: temperature, controlled before 1930 in 52 per cent of the cases and after in 69 per cent; aeration, controlled 38 per cent before and 40 per cent after 1930; and velocity, controlled in 33 per cent of the cases before and in 52 per cent after the beginning of 1930.

## Atmospheric Corrosion Tests

After reviewing the procedures in laboratory and field tests which have been adopted by the various agencies conducting such tests, H. S. Rawdon[51] recommends the following in any consideration of an attempt at standardization of such tests.

1. The results of atmospheric field exposure tests should always be correlated with the prevailing atmospheric conditions at the test location, particularly the degree of pollution of the air, and the season at which such tests are started.

2. A close distinction must be drawn between tests carried out for obtaining basic data on what are essentially the chemical characteristics of the material and tests having as their aim the acquisition of engineering corrosion data. The testing procedure, size of specimen, method of inspection, etc., usually differ widely in the two cases.

3. Laboratory tests are usually carried out for a specific purpose. Their indications with respect to the serviceability of any material should be confirmed by field tests which latter, however, are not to be regarded as necessarily identical with service.

4. A relatively large surface area with respect to the mass of the specimen is always advantageous for atmospheric corrosion tests. When the progress of corrosion is to be followed by change-of-weight determinations, a large area : weight ratio is required. This practically limits such tests to sheet or similar material.

5. For field exposure tests, the specimen should be supported on rigid permanent supports in such a manner that no specimen is influenced through contact, rain drip, or otherwise, by another specimen or by the supports used; supporting points for specimens should be restricted to contact with inert non-metallic materials; exposure should be toward the south at an angle of 30 to 45 deg. with the horizontal; and a distinction should be made between the results obtained on the lower and on the upper surfaces of the specimens.

6. The frequency of observations must be determined by the purpose in view, the nature of the material and the environment. Inspections at shorter intervals are always advisable during the early part of the test.

7. Definite uniform nomenclature or descriptive terms used in describing the appearance of corroded specimens should be adopted and, wherever possible, the results of visual inspections should be expressed by a numerical rating.

8. Recommendations concerning methods which are satisfactory for cleaning specimens prior to weighing are very desirable. Such methods will vary with the accuracy desired and the purpose of the test.

9. The precision used in making change-of-weight determinations must be varied to suit the purpose of the test. Weight determinations to 0.01 ± .005 g. are entirely satisfactory for a great deal of the work of this kind. All changes in weight should be calculated on the basis of unit of area and unit of time. The unit, mg/sq. dm./day, which has been suggested is not very satisfactory for ordinary atmospheric corrosion test with respect to the unit of time. The conversion of change-of-weight data into units of "penetration per year" is not so necessary and helpful in atmospheric corrosion tests as in other forms of corrosion testing.

10. Change-of-strength determinations should preferably be made on specimens machined from material after it has been corroded than on specimens which have corroded after being machined. A change in ductility is a more sensitive indicator of the effect of corrosion than the accompanying change in tensile strength. Tests of this kind are essential for evaluating properly the corrosion behavior of certain types of metallic materials.

11. The type of specimen and assembly used by A.S.T.M. Committee B-3 in the study of galvanic corrosion under atmospheric conditions is probably the most satisfactory that has been used for this purpose.

*(Continued on page 26)*

# THE ESTIMATION OF

# Inter-Granular Surfaces and Volumes

# IN METALS

by Herman F. Kaiser

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THE GRAIN BOUNDARY SYSTEM of a metal has always been a fascinating subject for speculation as well as for study, but it has actually received far less attention than the bulk of the metal itself. In recent years certain lines of study have been bringing about an ever keener interest in this subject. The intercrystalline brittleness and corrosion of metals, fatigue failure possibly resulting from micro-cracks in and between the grains, recrystallization and grain growth, precipitation hardening and Widmanstätten structures, postulated imperfect or mosaic structures in crystals, are some of these special interests which have increased the importance of this subject.

The grain boundary is more than a fictive surface of separation between the grains but is rather the seat of complicated atomic and macroscopic conditions. The most obvious characteristics of the grain boundary are: (1), a surface extent, and (2), a volume extent. We may ascribe to the grain boundary a volume for even in the purest metal the grain boundary is a region in space where the atomic order can hardly be perfect due to the diverse orientations of neighboring grains. At the other extreme in purity we may have the grain boundary composed of a thick film of an impurity or a second phase.

While much qualitative information on the grain boundary has been obtained, quantitative data are not so easily obtained because the grain boundary is such an irregular thing that only a statistical or an approximation method of approach is open to us. It is the aim of this paper to develop such a method.

In pure metals and many alloys the grains have a quasi-geometric structure and it seems possible to at least approximate a crystal aggregate of this type by a model metal in which the grains are all small, regular, equal-sized space-filling polyhedra. Fig. 1 shows how such an aggregate may be built out of space-filling cubo-octahedra. Fedorov[1] showed that any crystalline medium could be considered as built up of a large number of small, equal solid figures and by limiting the kinds of these polyhedra to only those bounded by plane faces, found that there were essentially only four basic kinds of space-filling parallelohedra—the

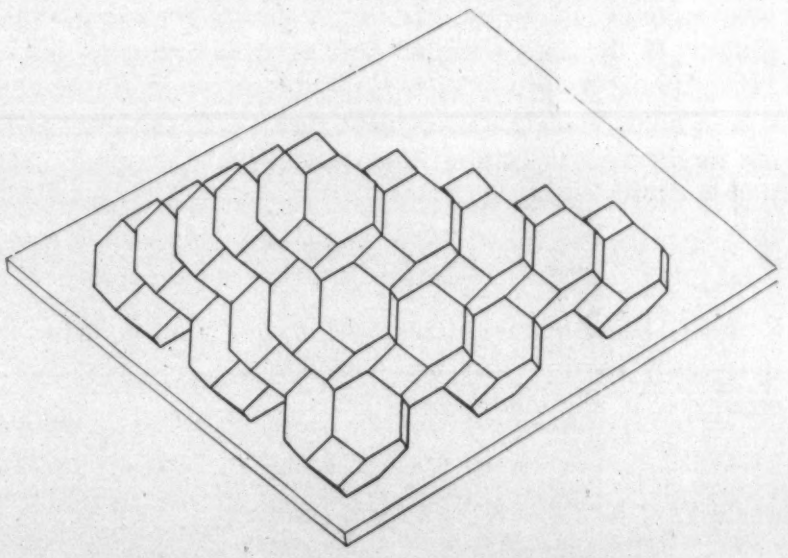
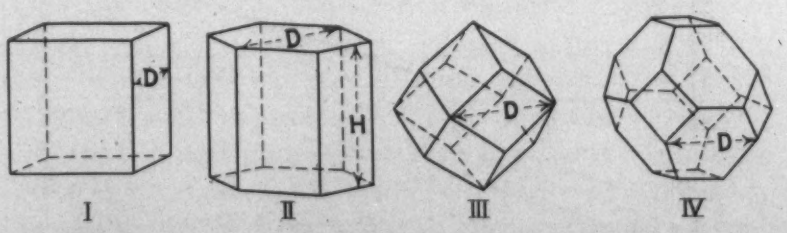


*Fig. 1.—Aggregate of Cubo-octahedra.*

cube, the hexagonal prism, the rhombic dodecahedron and the cubo-octahedron of Lord Kelvin. (See Fig. 2). From these other space-filling forms may be derived, as for example, the cube may be deformed into a rectangular paral-

*Fig. 2.—Parallelohedra of Fedorov.*




lelopiped or into a rhombic prism and still be a space-filling form.

In Table I are given the volume and surface character-

| Type of Unit Grain | $V_g$ Volume per grain | $A_g$ Intergranular area per grain | $A_g/V_g$ Ratio | $V_b$ Intergranular Vol./cc $T \ll D$ | $V_b$ Intergranular Vol./cc $T \leqq D$ |
|---|---|---|---|---|---|
| I Cube | $D^3$ | $3D^2$ | $\frac{3}{D}$ | $\frac{3T}{D}$ | $(1-ND^3)$ |
| II Hexagonal Prism | $0.6495 \cdot D^2H$ | $0.6495D^2+1.5DH$ | $(\frac{1}{H}+\frac{4}{\sqrt{3}D})$ | $(\frac{1}{H}+\frac{4}{\sqrt{3}D})T$ | $(1-0.6495ND^2H)$ |
| III Rhombic Dodecahedron | $0.7071 \cdot D^3$ | $2.1213D^2$ | $\frac{3}{D}$ | $\frac{3T}{D}$ | $(1-0.7071ND^3)$ |
| IV Kelvin Cubo-octahedron | $1.414 \cdot D^3$ | $3.350D^2$ | $\frac{2.37}{D}$ | $\frac{2.37T}{D}$ | $(1-1.414ND^3)$ |
| | (1) | (2) | (3) | (4) | (5) |

*Table I—Properties of Space Filling Polyhedra.*

istics of each of these types of parallelohedra. The first column gives the volume of the grain in terms of a representative grain diameter D which has to be arbitrarily chosen in each case. The second column likewise gives the surface, and the third column the ratio of volume to surface. The fourth column gives the volume of the intergranular film when the film has a thickness $T$ which is small, compared to the diameter D of the grain. The fifth column gives the volume of the intergranular film when the film thickness is comparable to the diameter of the grain. In this case an exact expression for the film volume can only be set down if the actual number N of grains per cubic centimeter of model metal is known.

In Table I the characteristics of these forms were given in terms of an arbitrary diameter D selected in each case. In order to compare the space-filling properties better, some way not involving D should be used and this may be done by making use of N, the number of grains per cubic centimeter. If the intergranular film is infinitesimally thick, N is also the reciprocal of the volume of one grain of any type. From Table I it is evident that (with the exception of the hexagonal prism) the quantities $V_g$ and $A_g$ are simply expressed by equations

$$V_g = KD^3 \quad (1)$$
$$\text{and } A_g = K'D^2 \quad (2)$$

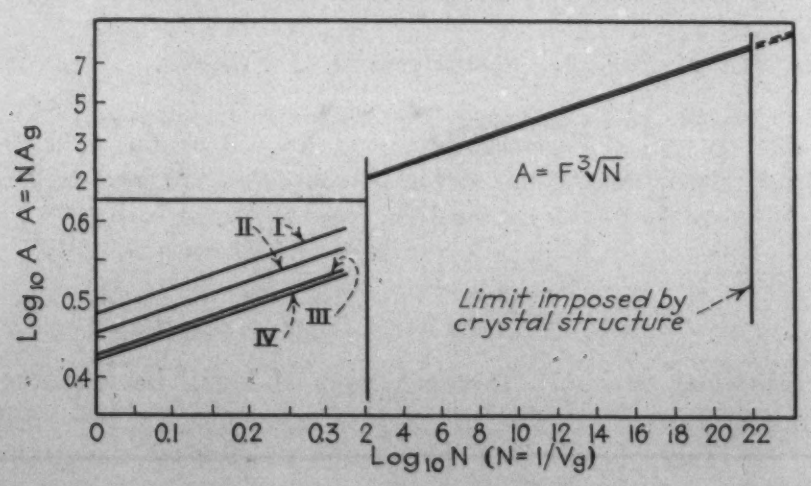
K and K′ being numerical constants to be found in Table I. It is easily shown* that the intergranular area per cubic centimeter of the model metal is

$$A = NA_g = F\sqrt[3]{N} \quad (3)$$

where $F = K^{-2/3}$. K′ is a form constant.

* Eliminate D from (1) and (2). Express $A_g$ in terms of $V_g = \frac{1}{N}$, K, and K′. Multiply by N.

*Fig. 3.—Intergranular Area A in Terms of $N = 1/V_g$.*




The hexagonal prism may be treated like the other types for the special case D = H. Using this special case, the intergranular area per cubic centimeter constants of the four basic types of unit parallelohedra are:

$$F_I = 3{,}000;\ F_{II} = 2{,}866..;$$
$$F_{III} = 2{,}673...;$$
$$F_{IV} = 2{,}659... \quad (4)$$

where the subscripts refer to Types I, II, III and IV of Fig. 2, and Table I. The ratios of these factors will represent the ratios of the intergranular surfaces of the types of model grains at any chosen value of N. Equation (3) may be put into the equivalent logarithmic form:

$$\log A = 1/3 \log N + \log F \quad (5)$$

In Fig. 3 curves of this equation are plotted for each of the four types of grains from N= 1 to N = $10^{22}$. In order to show separated curves for the four basic types the curves are plotted on a magnified scale in the lower left hand corner. Here it may be seen that the cubic grain has the greatest inter-granular area per cubic centimeter, the next is the hexagonal prism (for the special case D = H) followed in order by the rhombic dodecahedron and the cubo-octahedron. The last one (Type IV) was considered by Lord Kelvin[2] as representing that form of space-filling polyhedron possessing a minimum of partitional area. This fact allows further conclusion on what type of model grain will best represent an average real metallic grain. In actual cases the grains are not of the postulated ideal shape and may even possess curved and re-entrant surfaces. Therefore, it is unlikely that the intergranular area per unit volume of a real metal be anything but greater than that of a Type IV grain.

Mathematical difficulties attending calculations on parallelohedra with curved surfaces make it hard to approach this point more closely. On the other hand we know that grain structures are seldom cubical (as in the dendrites of bismuth) and this leads one to feel that the cubical type of grain gives the maximum possible intergranular area per unit volume. Therefore, real grains should be best approximated by model grains of Types II and III. Furthermore, the relative values of the factor F give an idea of the error involved should the intergranular area per unit volume be a minimum. If the cubic model is used, the error in A is

$$\frac{3{,}000 - 2{,}659..}{2{,}659..} \times 100\% = 12.8\%$$

For Types II and III the errors are 7.8 per cent and 0.53 per cent, respectively, and it is safe to say that the intergranular surfaces in real metals can be estimated to a part in 10 at worst and, with careful judgment, to a part in 50 or even better providing N, the number of grains per unit volume, be known accurately enough.

Unfortunately, the determination of N or $V_g$ is not as direct and accurate as one could wish. The metallographer determines not N but a quantity, S = a/n*, or the mean sectional area per grain. This quantity is statistically related to N. Although this relation is not known, a rough, round number relation between the mean grain volume and the grain size S has been given by Gulliver.[3]

* a is an arbitrary sectional area in which n grains are counted.

$$V_g = 3/2\ S^{3/2} \qquad (6)$$
$$\text{or } N = 2/3\ S^{-3/2} \qquad (7)$$

E. Scheil[4] and others have been engaged with the problem of determining the mean grain volume assuming the grains represented by an aggregate of packed spheres. More recently Scheil[5] has devised direct microscopic statistical methods for determining the mean grain volume and found the solution given by the spherical grain assumption to be appreciably in error. (X-ray Laue pictures may be employed to determine N but the method suffers certain drawbacks too.)

Returning to Fig. 3, the curves indicate that the intergranular area increases indefinitely as the grain size diminishes. Yet the grain size cannot actually become smaller than the parameter of the atomic lattice which is around $5 \times 10^{-8}$ corresponding roughly to $N = 10^{22}$. The actual limit, however, is to be found at much smaller values of N. The sizes of the blocks in mosaic structures have been quoted[6] as being around $10^{-14}$ cu. cm. in volume corresponding to $N = 10^{14}$. The magnetic "domain" or "Bitter"[7] patterns give even larger values, $10^{-12}$ cu. cm. corresponding to $N = 10^{12}$. It thus seems unlikely that the intergranular area in metals can be greater than $10^5$ sq. cm. per cu. cm. of metal.

Having set up an expression for the intergranular area per cu. cm. of the model metal in terms of the grain number $N = 1/V_g$ general expressions may be set up for the volume of the intergranular film. If the film is thin the intergranular volume (per c.c.) is simply $V_b = A\ T$ where $T$ is the film thickness. When the film is thick, this becomes inaccurate and the only precise expression is one giving the difference between the total volume and the volume actually occupied by the grains. We thus have the two self evident equations:

$$V_b = AT \qquad (T << D) \qquad (8)$$
$$V_b = (1 - NV_g) \qquad (T \leqq D) \qquad (9)$$

Now it is very desirable to relate $V_b$ to the density and composition of the metal and this may be done from the following considerations: Letting $c_b$ be the fraction of the total weight (wt. %/100) due to grain boundary material and s the weight fraction in solid solution in the matrix metal the mass of grain boundary material present *in the grain boundaries* in 1 cu. cm. of metal is simply

$$c_b\rho - s \cdot \rho = (c_b - s)\rho$$

where $\rho$ is the density or mass of 1 cm.$^3$ of the metal. This quantity must be equal to $\rho_b\ V_b$ where $\rho_b$ is the density of the intergranular material. Thus

$$\rho\ (c_b - s) = \rho_b \cdot V_b \qquad (10)$$

which may with substitutions from (3), (8) and (9) be solved for $c_b$ giving the two expressions:

$$c_b = s + \rho_b/\rho\ (F\ N^{1/3}\ T) \text{ (thin films)} \qquad (11)$$
$$C_b = s + \rho_b/\rho\ (1 - NV_g) \text{ (thick films)} \qquad (12)$$

A fairly practical application of these equations is the estimation of the relative amount of insoluble impurity ($c_b - s$) of an intergranular substance such as an oxide or sulphide which will be required at any given grain size to form a complete envelope of any small thickness $T$ about the grains. The writer is not trying to give the impression that such films exist in general but rather to judge from

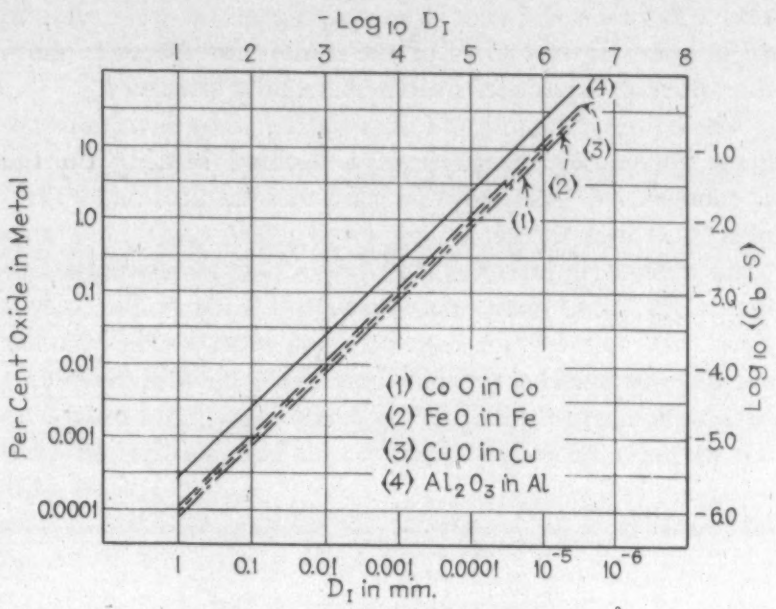



*Fig. 4.*

straightforward considerations what the concentrations and grain sizes would have to be in order that such films might exist. That they actually exist in many cases cannot be gainsaid and it remains for experimental work to determine whether or not submicroscopic films exist in the grain boundaries of quite pure metals.

Fig. 4 shows some curves for equation (11) plotted in logarithmic form which show the amounts of insoluble oxides which might exist in a layer of thickness $T = a_o$ (parameter of the oxide crystal structure) for any particular grain size. The oxides are the simplest oxides of the metals Co, Fe, Cu, and Al and for ease of calculation the cubical type of grain structure ($F_1 = 3$) was assumed. On the ordinate and abscissae scales are given the corresponding percentage of insoluble oxide and the grain diameter. These different metals have curves running fairly closely in spite of their different natures. It may be noted that when the grain size is around 0.1 mm. 0.001 per cent of insoluble oxide is all that is required to form this hypothetical film. An actual film would not be likely to have this minimum thickness but rather some multiple ranging from 10 to 100 or even more. Correspondingly the amount of insoluble oxide would be increased from 0.001 per cent to 0.01 or 0.1 per cent. G. Derge[8] has recently concluded from theoretical studies that a stable crystal nucleus need not contain more than 100 atoms and that probably 10 atoms are sufficient. This tends to support the idea that a stable intergranular oxide film of thickness 10-50 $a_o$ may exist and such a film in metals having a grain size around 0.1 mm. would require 0.01 to 0.05 per cent insoluble oxide.

Recently Northcott[9] has advanced the view that the boundaries of the mosaic blocks are the seats of precipitation phenomena as shown by veining and sub-boundary effects. Taking again the size of the mosaic blocks as being around $10^{-4}$ cm. Fig. 4 indicates that at least 0.10 per cent of insoluble oxide must be present to completely cover the blocks with a layer one $a_o$ thick. If the block size is $10^{-5}$ cm., 1 per cent will be required or if a stable film has a thickness of 10 $a_o$, 1 per cent of oxide will be required to completely cover blocks of $10^{-4}$ cm. size. It thus seems that a complete precipitation of the type postulated by Northcott calls for a greater percentage of oxide than is actually found in most steels and indeed the figures he observed were awkwardly too large to be explained in this way. His views

may still be correct if it is assumed that the precipitation takes place on only some of the mosaic interstices to form the larger precipitation structures actually observed.

The nature, amounts and distribution of impurities in the grain boundaries should have a decided bearing on the phenomena of grain growth and recrystallization. Tamman,[10] in his theory of recrystallization, has held that grain growth is hindered and controlled by envelopes of impurities in the grain boundaries. A study of Fig. 4 will show that, as the grain size increases, more oxide becomes available to thicken the intergranular film and thus perhaps to increase the barrier to grain growth. Space does not permit a thorough discussion of recrystallization phenomena from the standpoint of the material of this paper. This subject will be treated by the author in a separate paper.

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*(Continued from page 22)*

## Alternate Immersion and Water-Line Tests

D. K. Crampton[52] describes the alternate immersion and water-line tests in use at the laboratories of the Chase Brass & Copper Co. In general, the results obtained by the alternate immersion test have indicated relative rates of corrosion of several alloys which are very nearly in line with relative behavior of these same alloys under generally similar service conditions. They have found that with the less corrosive solutions, 100 days give good results with most metals; with moderately corrosive solutions, 30 days; and for the highly corrosive solutions a test period of only a few days is required. Tensile strength specimens are used. To stimulate "deposit attack," a piece of cord is held against the middle of each side of each specimen, normal to the long dimension. The specimens are carefully examined under a binocular microscope after corrosion, and the type of attack carefully considered. The alternate immersion test, particularly when using the cord against the surface of the specimen, gives much greater corrosion rates than will be experienced in service conditions where the metal is entirely immersed in the solution. Localization of attack takes place at the cord also, which would not occur in practice except where deposit attack due to foreign materials resting on the surface of the metal is encountered. As far as possible, the alternate immersion test should be run in connection with other tests, including service tests if possible, in order to confirm the results obtained. The water-line test is also used and the results applied to service conditions where water-line attack is a factor.

## Salt Spray Testing

The salt spray test was originally developed as a simulation of seacoast atmosphere in the study of protective coatings. Its fundamental simplicity, being merely the exposure of samples in a closed chamber to a mist from a salt solution, made its investigation desirable provided that its reproducibility was adequate and its correlation with results from actual service, accurate. Its simplicity was deceptive. Variation in spray, distribution of spray in the chamber, composition of the spray, and temperature were variables that were not easily controlled and the results obtained were erratic, particularly when it was attempted to compare results from one laboratory with those from another. Considerable controversy resulted which still continues. Dix and Bowman[49] report data on the same material from a number of spray boxes with very uniform results. Their long experience with salt spray testing leads them to the conclusion that the results can be made reasonably reproducible and are of substantial value when properly interpreted. "For comparison of similar materials or as an an acceptance test for certain classes of materials, the test has much to recommend it. For comparisons of radically different materials (specifically, different base metals) or as an accurate indication of service life in other than marine atmospheres, its use may be hazardous."

## Soil Corrosion Tests

Soil corrosion testing before 1922 had received comparatively little attention. Since that time however the activities of the National Bureau of Standards and of interested industrial firms have produced a very considerable amount of data and have resulted in notable progress. Logan, Ewing and Denison[54] discuss the factors to be considered in such testing which involves particularly the corrosiveness of the soil, the relation between pit depth and area, and the relation between pit depth and time. They have developed empirical equations in which the depth of pit is expressed as power functions of time and exposed area, the constants of the equations being related to the properties of the soil. The slope of the pit depth-time curve when plotted on logarithmic coordinates is shown to be determined largely by the aeration of the soil, the more poorly aerated the soil the steeper the slope.

## Standardization

Standardization of corrosion tests is a question to be carefully considered. Where such tests are used as acceptance tests, standardization seems advisable, particularly where results from different laboratories are to be compared. Theoretical investigations should not be hampered by such limitations. It should, nevertheless, be emphasized that, if trustworthy results are to be obtained, significant factors must be controlled and all data as to the conditions of the investigation be recorded to enable the correlation of results of different investigators.

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